LA LIQUEFACTION
DE LA
CANADA
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INTRODUCTION

These proceeding are the result of the 3rd liquefaction experts workshop held at the University of Sherbrooke on the 28 & 29th September 1983. Though named the 3rd meeting, this is infact a misnomer because it was the 4th meeting in a series that started at the 29th CSChE meeting held in Sarnia Ontario September 30 to October 3, 1979. The 2 subsequent meetings were held under the auspices of the ENFOR programme. The first at the University of Toronto in August 1980 and the second at the University of Saskatchewan in February 1983. Each of these meetings marked the begining of a new phase in the advancement of biomass and peat liquefaction. The Sarnia meeting belonged to an era when biomass liquefaction was viewed more on less as part of coal liquefaction. By the Toronto meeting the extraordinary reactivity of biomass in batch processes was recognised and this pointed to the need for semi continuous and continuous processes.

At the Saskatoon meeting the preliminary results for continuous and semi-continuous processes were available along with the first detailed analytical chemistry results on the product oils. The Saskatoon meeting and the Sherbrooke meeting encompass the activities of the International Energy Agency BLTF study.

The IEA collaboration: a project known variously as CPD1 or IEABLTF, was a cooperation between 4 countries: the USA, Canada, Sweden and Finland as part of the Forestry Energy Agreement-group D-biomass conversion topic. In this project there were 3 components; one of these, a series of comparative tests included many of teams whose papers are in these proceedings. Each participating research group processed a Canadian Standard Wood and a Finish Peat under their process conditions and the product oils were subjected to analysis by a central laboratory.

These data are partially reported here by David Beckman who was the Canadian member of the IEABLTF working group. The full study comprising: a state of the art survey; the comparative tests; analytical results; upgrading studies and a techno-economic analysis will be published by the Swedish Operating agent in mid 1984.

This meeting under the auspices of the Canadian Federal Governments Energy Research and Development Program was organised by the National Research Council and the University of Sherbrooke. The international nature of these meetings was futher expanded by the participation of researchers from France who joined the now well established collaboration between groups in the USA, Canada, Finland and Sweden at this workshop. The 23 papers presented here, are a benchmark set in the evolution of our understanding of wood and peat liquefaction. While the papers are in themselves a record of work undertaken up to mid-summer 1983 they do not do justice to the many informal discussions that took place at Sherbrooke in the Fall of 1983. These we have tried to capture in the final notes provided at the end of the proceedings. The discussions in Sherbrooke point to the fact the biomass and peat liquefaction is moving from the status of an "art" to that of a science with application not only in energy but also materials and chemicals production.

As with all workshops and meetings, their successful conduct depends on the actions and effort of many persons. The University of Sherbrooke organising committee composed of representatives of the administration and the faculties of science and engineering -Madame J. Lasalle, M. J. Louis Lareau, Madame A. McGee, Professors, C. Roy, M. Ménard, E. Chornet are to be thanked for their efforts, organisation and hospitality, which facilitated the dialogue that took place.

I also would like to thank the 4 secretaries Ann McGee, Sylvie Carrignan at Sherbrooke and Jean McNulty and Murielle Plouffe, at NRC for their enthusiasm and patience in assisting us with the meeting arrangements and in the production of these proceedings.

R.P. Overend
Bioenergy Division
National Research Council

Section 1

THE INTERNATIONAL ENERGY AGENCY COMPARATIVE TEST PROGRAM

RESULTS OF THE COMPARATIVE TEST PROGRAM

BY DAVID BECKMAN

IEA BIOMASS LIQUEFACTION TEST FACILITY PROJECT

As part of the International Energy Agency, Biomass Liquefaction Test Facility (BLTF) Project, a comparative test program was organized whereby all laboratories currently active in biomass liquefaction were supplied with standard feedstocks of wood and/or peat. The researchers at each facility were instructed to run the feedstock under their process conditions. A common feed material was used to eliminate the differences in results due to the use of different feedstocks. The objective of the program was to provide a basis for process comparison that could be used, together with the other findings of the BLTF project, to identify the most promising biomass thermochemical conversion routes.

Processes aimed at maximizing liquid yields were considered for the program. The following laboratories agreed to participate in the test runs:

1. BC Research, Vancouver, Canada
2. Georgia Institute of Technology, Atlanta, USA
3. Royal Institute of Technology, Stockholm, Sweden
4. Université de Sherbrooke, Sherbrooke, Canada
5. University of Saskatchewan, Saskatoon, Canada
6. University of Toronto, Toronto, Canada
7. University of Waterloo, Waterloo, Canada
8. University of Arizona, Tucson, USA
9. Technical Research Center of Finland, Espoo, Finland

The conversion methods studied at these facilities included vacuum and atmospheric pyrolysis, high pressure catalytic and non-catalytic liquefaction, and supercritical extraction. The final two laboratories on the above list, the University of Arizona and the Technical Research Center of Finland did not conduct conversion tests but studied high pressure biomass feeding techniques.

The standard wood feedstock was supplied by the Ontario Ministry of Natural Resources. It was a 7 year old hybrid poplar (Populus Deltoides) from a plantation in Eastern Ontario, Canada. The plantation was managed under

the Farming Fast Growing hardwoods program that has an objective of developing high-yielding, hardwood plantations. The harvested logs were debarked, chipped, and dried slowly at room temperature to 10% moisture content. The analytical details are given in Table I

Table I. Standard Poplar Wood Feedstock

Clone:	D38 (a Populus Deltoides clone with Ontario Parentage)
Age:	7 Years (planted 1976)
Date Harvested:	December 15-17, 1982
Location:	Brockville, Ontario, Canada
Longitude:	75 40 W
Latitude:	44 35 N
Elevation	300 A.S.L.
Average Height:	12.12 meters
Average Diameter	12.34 centimeter (at breast height)

Ultimate Analysis:

Element	% by Weight
Carbon	44.5
Hydrogen	5.2
Oxygen	49.8
Nitrogen	0.07
Ash	0.4

Higher Heating Value: 19.5 MJ/kg

Other Analyses:

Component	% by Weight	Method
Extractives	3.0	Tappi T12 Os-75, oven dry basis
Lignin	24.2	Acid insoluble - Tappi T222 Os-74 Acid soluble - Tappi UM 250 Extractives-free, oven dry basis
Pentosan (Hemi cellulose)	20.5	Tappi T223 Os-71 Extractives-free, oven dry basis
Cellulose	55.3	By difference
Ash	0.5	By difference, oven dry basis

The standard peat feedstock, supplied by the Technical Research Center of Finland, was from a bog located 60 km south of the city of Oulu, Finland. The bog is a milled peat production site. It was drained in 1976 and put into production in 1978.

The results of analysis of the peat by the Technical Research Council of Finland are shown in Table II.

Table II. Standard Peat Feedstock

Component	Results/Units
Total moisture content at arrival	51.0 % w/w
Ash content for dry matter	4.67 % w/w
Volatiles for dry matter	68.1 % w/w
Gross heat of combustion for dry matter	23.08 MJ/kg
Net heat of combustion for dry matter	21.98 "
Net heat of combustion at arrival	9.53 "
Carbon content for dry matter	54.3 % w/w
Nitrogen content for dry matter	1.78 "
Hydrogen content for dry matter	5.05 "
Sulphur content for dry matter	0.23 "
Ash analysis for dry matter:	
SiO_2	399 mg/g
Al_2O_3	119 "
Fe_2O_3	276 "
CaO	83 "
K_2O	6 "
P_2O_5	4 "
MgO	23 "
Na_2O	1.2 "
SO_3	5.6 "

At the time of the Third Liquefaction Specialists meeting the test runs had been completed at all of the facilities except the Georgia Institute of Technology, and the University of Arizona. Detailed results of the runs completed thus far can be found in the papers in this volume.

Comparisons of these results are difficult due to the differences as to the extent of development of the biomass conversion processes in each laboratory. Only the University of Waterloo flash pyrolysis and the Université de Sherbrooke vacumm pyrolysis processes were at a state of nearly complete optimization. All of the other processes were not optimized at the time of the test runs.

Differences also existed in the operating experiences of the laboratory conversion units. At the time of this project many laboratories had recently changed from batch or semi-continuous to fully continuous systems. Only a few preliminary runs could be made on these units before the test runs. These facilities include: University of Toronto, Université de Sherbrooke: (High Pressure Liquefaction), University of Saskatchewan, and the Georgia Institute of Technology. The lack of operating experience caused problems at the Georgia Institute of Technology that have delayed the completion of the test runs.

Examination of the oil yields from the different test runs using the wood feedstock shows that high yields of 65-70% can be obtained under a number of very different conditions. Figure 1 and Table III illustrate that both pyrolysis in a gas phase at atmospheric pressure, as in the Waterloo pyrolysis process, and pyrolysis in a liquid phase, with hydrogen present, at a pressure of 8.3 MPa, as in the Sherbrooke liquefaction process, lead to high liquid yields.

Table III: Comparison of Product Yields: Wood Yields (maf)

	percentage			
	Oil	Gas	Water	Char
Vacuum Pyrolysis	44.7	12.4	13.7	29.3
Flash Pyrolysis	68.8	12.3	7.5	11.7
Catalytic Liquefaction (Toronto)	19.4	47.2	na	2.0
Hydropyrolysis (Toronto)	53.4	6.4	39.0	1.2
Liquefaction (Sherbrooke)	68.0	~10	na	1.2
*Supercritical Extraction	42.7	6.8	9.1	2.8
Liquefection (Saskatchewan)	39.1	22.1	na	0.1

na = not available

*Note: The oil products are know to contain acetone condensation products [McDonald, Bennett and Howard, these proceedings] and are thus an overestimate of productivity.

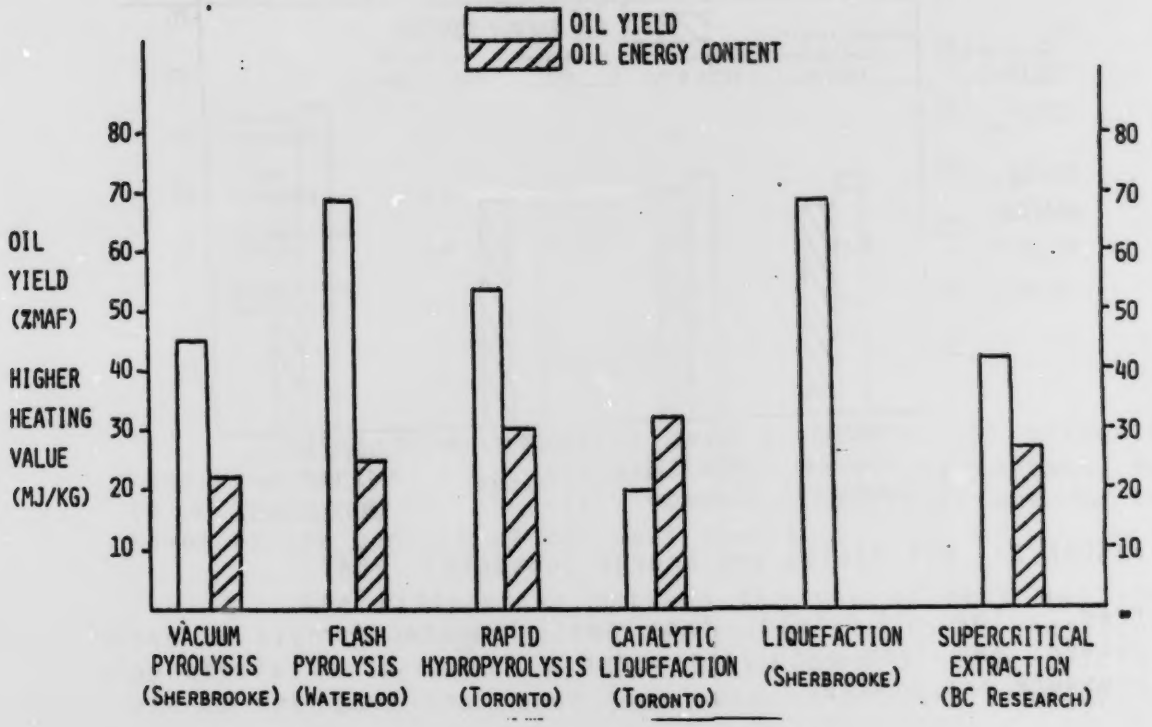

FIGURE 1: Oil Yields and Energy Contents: WOOD

The lower oil yields in the other processes are compensated for by the by-product yields as can be seen in Table I. In vacuum pyrolysis the lower oil yield is in addition to a higher char yield, and for rapid hydropyrolysis there is a high aqueous phase organics yield.

Figure 2 and Table IV show that similar oil yields can also be attained under different processes with peat as

Table IV: Comparison of Product Yields: Peat Yields (maf)

	Oil	Gas	Water	Char
Vacuum Pyrolysis	40.1	15.5	10.3	34.2
Flash Pyrolysis	41.3	12.1	7.6	38.9
Liquefaction (Sweden)	40.2	18.0	27.7	17.4
*Supercritical Extraction	55.3	na	na	54.6

*Note: The oil products are know to contain acetone condensation products [McDonald, Bennett and Howard, these proceedings pages] and are thus an overestimate of productivity.

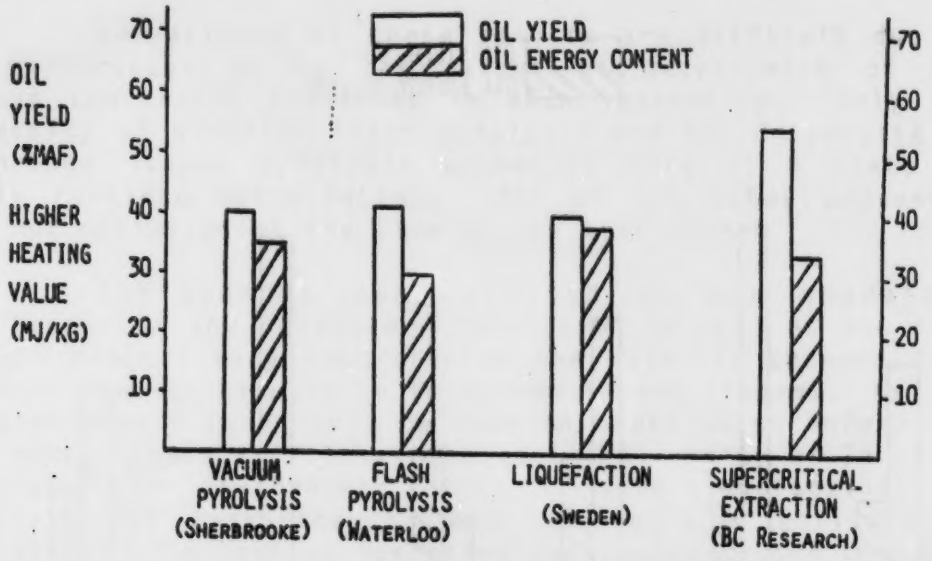

FIGURE 2: Oil Yields and Energy Contents: PEAT

feed. The oil yields from peat liquefaction in a donor solvent and from pyrolysis under a vacuum or at atmospheric pressure are similar.

Oil properties for wood and peat are compared in Tables V and VI. All of the product analysis results were not available at this time. Generally, the oils produced from the vacuum and flash pyrolysis processes using the wood feed are lower in energy content, due to a higher oxygen value, than oils produced under higher pressures. The vacuum and flash pyrolysis oils have lower viscosities due to their higher water contents.

Table V: Comparison of Oil Properties: WOOD

	% H_2O in Raw Product	Pour Point (°C)	Viscosity (cP @ 40°C)	Higher Heating Value (maf) (mJ/kg)	wt % Oxygen (maf)
Vacuum Pyrolysis	37.6	-12	5	22.1	31.1
Flash Pyrolysis	24.3	-24	40	24.3	28.0
Catalytic Liquefaction (Toronto)	9.4	19	3000	31.8	18.3
Supercritical Extraction	14.1	-24	unk	27.8	23.7
Liquefaction (Sherbrooke)	(not available)				
Hydropyrolysis (Toronto)	(unknown)				24.7

Table VI: Comparison of Oil Properties: PEAT

	% H_2O in Raw Product	Pour Point (°C)	Viscosity (cP @ 40°C)	Higher Heating Value (maf) [MJ/kg]	wt % Oxygen (maf)
Vacuum Pyrolysis	19.6	42	460	35.0	10.7
Flash Pyrolysis	6.9	31	8400	30.2	15.2
Liquefaction (Sweden)	0.0	[illegible]		34.8	18.3
Supercritical Extraction	16.2	44	280	33.0	14.4

Oils produced using peat are higher in viscosity than wood derived oils, but are higher in energy content, due to a lower oxygen content. This is partially due to the lower oxygen content of the peat feedstock.

The differences between the use of peat and wood can be seen by comparing the results of the flash and vacuum pyrolysis tests, which used both. Figure 3 shows that oil yields for peat are lower than wood. The lower yields are

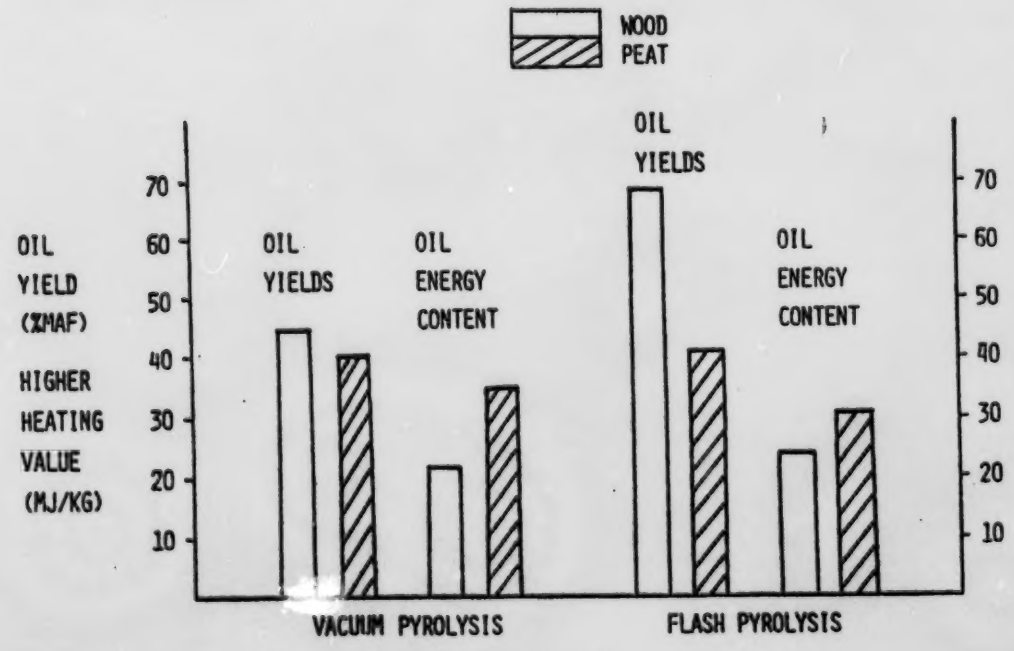

FIGURE 3: Comparison of Wood and Peat Results

compensated for by the higher char production. Gas and water yields are however, similar for both the feedstocks.

The preliminary results of the slurry pumping tests show that peat slurries can be pumped at higher concentrations than wood slurries in either a water or oil carrier. It also appears that a point exists at which further size reduction has no benefit on the pumpability of the material, and that higher solid concentrations can be pumped in oil than in water.

The results of the extrusion feeding test conducted at the University of Arizona were not available for this meeting.

The various problems encountered with the test runs at the different facilities have led to uncertainties in comparisons of the processes. But, regardless of these problems, the use of standard wood and peat feedstocks by the different research groups is beneficial. The major uncertainty in the effect of the feedstock on the conversion results has been eliminated, providing a basis for comparison. The use of standard feedstocks has made the results from the many processes given in these proceedings more useful to those interested in liquefaction.

Section 2

DIRECT LIQUEFACTION

CONTINUOUS REACTOR FOR THE LIQUEFACTION OF ASPEN POPLAR

R.L. EAGER, J.F. MATHEWS AND J.M. PEPPER
UNIVERSITY OF SASKATCHEWAN
SASKATOON, CANADA

INTRODUCTION

The liquefaction of a variety of lignocellulosic materials by reaction with carbon monoxide and water at elevated temperatures in the presence of sodium carbonate has been studied by several workers (Appell et al., 1971; Appell, 1977; Cavalier and Chornet, 1977; Elliott, 1980; Molton et al., 1981; Eager et al., 1981, 1982, 1983), as a means of preparation of a fuel oil to supplement fossil hydrocarbons. Some of these studies have been made using batch reactors in which the reactants and products are in contact under the reaction conditions of temperature and pressure for lengths of time which may be excessively long due to extended warming-up and cooling-down periods. The semi-continuous or continuous reactors used have involved the pumping of slurries of wood meal, water, and catalyst from atmospheric pressure to the reaction pressure of the order of 35 MPa. While such reactors enable the retention time at elevated temperatures to be shortened to a matter of minutes there is the attendant problem of pumping in a slurry against a high pressure gradient.

For the earlier work carried out in these laboratories on the liquefaction of aspen poplar wood (Eager et al., 1981, 1982) the use of a batch reactor meant that the reactants and products were held at temperatures between 573 K and 633 K for approximately 3.5 - 4 hours. Since initially the reaction mixture was highly alkaline (pH ~ 11) the opportunity for complex and severe side reactions to occur was greatly enhanced.

The next logical step in developing the wood-to-oil process was to design and construct a semicontinuous reactor. In this kind of reactor the wood meal could be fed continuously through a heated reaction zone where the reaction time at temperature could be controlled. On the other hand, the batch-charging of the wood meal to a pressured pre-reactor hopper would obviate the necessity to overcome pressure gradients. The design and operation of this semi-continuous reactor was discussed in a previous paper (Eager, Pepper and Mathews 1983). In this latter work it was shown that air-dried aspen wood meal could be converted into an oil in a yield comparable to that obtained in the batch process. The success of this semi-continuous

reactor was seen to be based on the utilization of a screw-type feed mechanism whereby a "plug" of highly compressed wood meal was maintained between wood supply and reaction zone permitting a pressure differential of up to 10 MPa to be maintained between the two.

It was decided to build a continuous reactor system, based upon this concept of a "plug", and utilizing a modified screw-type feeder mechanism, whereby air-dried aspen wood meal could be delivered from atmospheric pressure directly into a continuous tubular reactor operating at pressures up to 32 MPa. This paper describes the design and operation of this small-scale continuous reactor.

APPARATUS AND PROCEDURE

The continuous reactor has gone through a series of modifications. A schematic of the first continuous reactor is shown in Figure 1. The section to the right of section J-J is part of the original semi-continuous reactor and was described previously (Eager, Pepper and Mathews 1983). The continuous feeder unit consisted of a hardened tool steel housing into which was fitted a 316 stainless steel screw driven by a 1/2 HP motor coupled to a speed reduction gear box and a set of pulleys and a V-belt. The set of pulleys used gave a screw rotation speed of 7 rpm.

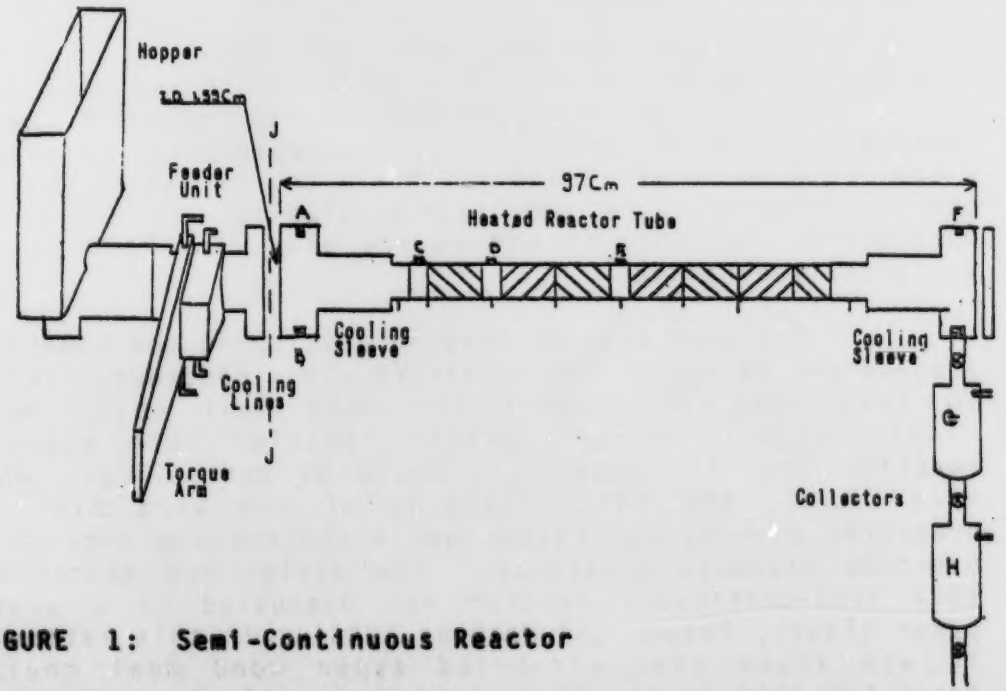

FIGURE 1: Semi-Continuous Reactor

To prevent torques being developed which could result in damage to the equipment an automatic shut-off was added. An arm, the "torque arm", is attached to the feeder unit housing which is free to rotate. The end of the torque arm bears against a spring loaded plate which in turn can contact a micro-switch and result in the electric circuit supplying current to the motor being opened. This unit is set to shut the reactor down when the torque reaches a value of 160 N-m.

In preliminary testing it was found that sufficient heat was generated in the feeder unit to raise the temperature to 90°C. It was also found that to be able to start the unit its temperature had to be in the 40-70°C temperature range. In order to be able to either heat or cool the feeder housing both the housing and the torque arm were provided with passages drilled in them and fitted with connectors so that cooling water, or warm water, could be directed through them. Heating could also be provided by a heating tape wrapped around the feeder unit housing.

A hopper, constructed of acrylic plastic, is used to contain a supply of wood meal. At the bottom of the hopper a screw with the ends having opposed pitches feeds the wood meal into the center of the hopper bottom where an opening allows the meal to drop onto the feeder screw. The hopper screw is driven by a small electric motor coupled to a speed reduction box through a pair of belt driven pulleys.

The auger in the reactor tube is threaded at the end nearest the feeder unit and screws onto the end of the feeder unit screw. Hence the 1/2 HP motor drives both the feed unit screw and the auger in the reactor tube.

The feeder unit must initially be loaded with wood meal without any back pressure in order to be able to form a plug and without unreacted wood accumulating in the reactor tube. To accomplish this the following start-up procedure is used. The reactor tube and auger are removed from the feeder unit. The hopper is filled with wood meal, the feeder housing heated to 40-70°C and the feeder unit started. The feeder unit is run for a sufficient length of time, approximately 15 minutes, until wood meal appears at the exit end of the feeder unit. The feeder unit is now filled with a solid core of wood meal which is capable of resisting the back pressure wich will be developed in the reactor tube. The auger is screwed into the end of the feeder unit screw and the reactor tube slipped over the auger and attached to the feeder unit.

In a typical run using Saskatchewan aspen wood meal the reactor was initially pressured to 13.6 MPa with CO and the feeder unit housing was heated to 40-70°C by use of a heating tape. The flow of the Na_2CO_3 solution, the flow of steam and the motor driving the feeder unit and the auger were all started at the same time. A 10% Na_2CO_3 solution was pumped in at port B at the rate of 6 mL/min and steam was added at port A at the rate of 8 g/min. CO was added through port E and exhaust gases were removed through valve K in order to maintain the reactor at the desired operating pressure of 17.7 MPa. Once the unit was started the heating tape was removed from the feeder unit housing and sufficient cooling water was used to maintain the housing temperature in the 40-70°C range. The electric heater on the reactor wall beween C and D was used to bring the reactant temperature to 360°C at D and the heaters between D and E were used to maintain 360°C in that region. Cooling water was run through the cooling sleeve on the downstream side in order to maintain the temperature at F at 125°C. Liquid product was removed from the bottom of collector H. At the end of 6 h it was decided to terminate the run. At that time the reactor was running smoothly and no difficulties were being experienced.

This first continuous reactor operated successfully using Saskatchewan aspen poplar wood meal, however difficulty was experienced when the I.E.A. hybrid poplar wood was used. After various unsuccessful attempts were made to use the hybrid poplar by varying the operating conditions the reactor was modified. The modification consisted of the construction of a new feeder unit and a new reactor. All of the other components used in the first reactor were retained. A schematic of the modified reactor is shown in Figure 2.

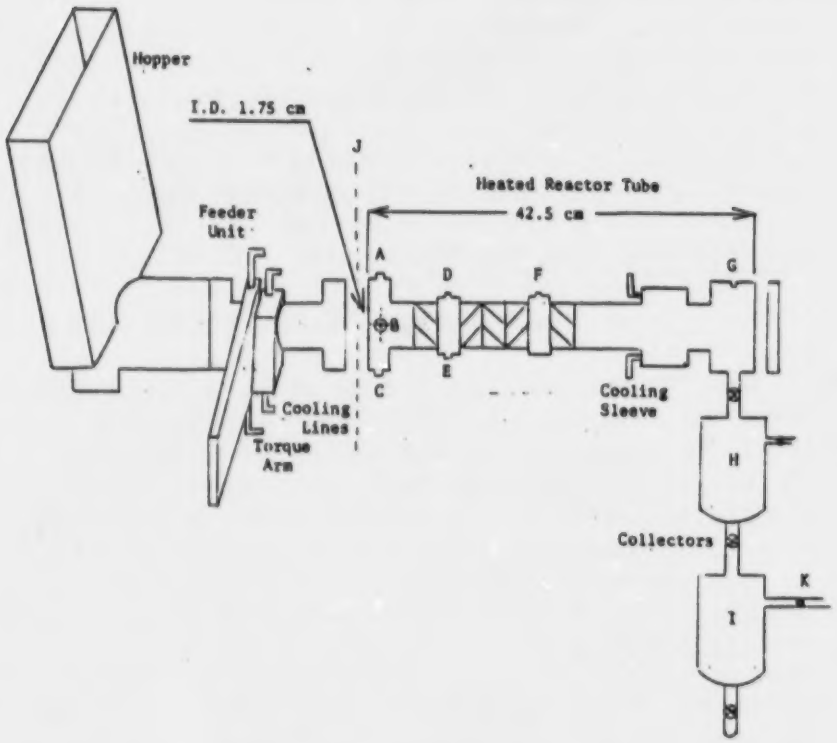

FIGURE 2: Modified semi-continuous rector

The diameters of the new feeder screw and reactor auger were 0.159 cm greater than in the first reactor. The feeder screw was hardened tool steel and the reactor tube and reactor auger were 316 stainless steel. These changes resulted in greater strength and increased resistance to wear. The feeder housing used in the first reactor was retained except that it was honed to accommodate the larger screw. The length of the new reactor is 42.5 cm, which is one half the length of the first reactor. Three infection ports are present in the flange used to connect the reactor tube to the feeder unit. There are three additional injection ports, two located 5.1 cm downstream from the flange and the third one 12.7 cm downstream from the flange.

An important modification of the reactor auger was an increased size of the groove at the upstream end. Tests had shown that the hydrid poplar was less compressable than Saskatchewan aspen poplar. Apparently the addition of water at the upstream end of the reactor resulted in such an increased volume of the reaction mixture due to the swelling of the wood that the torque increased sufficiently to stall the reactor. The increased size of the auger groove prevented this stalling from occurring.

RESULTS AND DISCUSSIONS

a) Saskatchewan aspen poplar wood meal as feed

In the run cited above a total of 1540 g of wood was fed to the reactor, the average feed rate being 4.28 g/min. A water-to-wood ratio of 3.3:1 and a Na_2CO_5-to-wood ratio of 0.15:1 were used. A total of 816 g of wet oil was collected which was found to contain 34.4% water. The result was therefore 535 g of dry oil which corresponded to a yield of 35% on a dry wood basis. An analysis of the oil showed 68.5% C and 6.7% H. The measured higher heat of combustion was 31.9 MJ/kg.

Some work has been done to vary the operating parameters of the process. Water-to-wood ratios as low as 2.5:1 and Na_2CO_3-to-wood ratios as low as 0.0125:1 have been used successfully. Reactor pressures from 15 to 32 MPa have proved operational with 32 MPa appearing to be the upper limit for the present screw-feeder design.

Nitrogen has been used to initially pressurize the reactor to 13.6 MPa; no CO was used in the reaction. This was a 6 h run, similar to that described in the section on Apparatus and Procedure except that a water-to-wood ratio of 2.5:1 was used and the Na_2CO_3-to-wood ratio was dropped from 0.025:1 to 0.0125:1 to 0.00625:1 at the ends of two hour intervals. For the total run 1593 g of wood meal had been fed to the reactor resulting in 667 g of dry oil or a yield of 42%. The product oil analysed 70.1% C and 6.5% H.

b) I.E.A. hybrid poplar wood meal as feed

i) Use of CO. The reactor was initially pressurized to 24.0 MPa with CO using port F. A 5% Na_2CO_3 solution was pumped in at port B at a rate of 4 mL/min and steam was added at port A at a rate of 8 g/min. The average feed rate of wood meal was 5.1 g/min, resulting in a water-to-wood ratio of 2.1:1 and a Na_2CO_3-to-wood ratio of 0.037:1. The rate of removal of exhaust gases through valve K was sufficient to maintain an operating pressure of 28.3 MPa. A total of 2600 g of wood meal was fed to the reactor. A total of 1480 g of wet oil was collected which was found to contain 34% of water. The result was therefore 975 g of dry oil which corresponded to a yield of 35% on a dry wood basis. An analysis of the oil showed 70.8% C and 6.5% H.

ii) Use of N_2. The same operating conditions were used as in i) except that N_2 to initially pressurize the reactor. A total of 2650 g of wood meal was fed to the reactor resulting in 1038 g of dry oil corresponding to a yield of 39.1% on a dry wood basis. An analysis of the oil showed 66.5% C and 6.5% H.

ACKNOWLEDGEMENTS

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UPDATE ON WOOD LIQUEFACTION STUDIES AT THE UNIVERSITY OF TORONTO

F. AGBLEVOR, D. CHOW, A. CHOWDHURY, M. HOLYSH, F. PORRETTA
AND
D.G.B. BOOCOCK

DEPARTMENT OF CHEMICAL ENGINEERING
AND APPLIED CHEMISTRY
UNIVERSITY OF TORONTO
TORONTO, ONTARIO, CANADA
M5S 1A4

INTRODUCTION

In the last year wood liquefaction studies have been focussed in four areas. These are liquefaction using a semi-continuous unit; liquefaction by rapid pyrolysis in water; chemical characterisation of oils as related to process parameters; and, lastly, upgrading of the oil products.

The major developments are as follows:

(a) The semi-continuous unit constructed under the ENFOR program was initially designed for catalytic liquefaction using nickel metal catalyst. Beckman (1981) of this group showed that catalytic liquefaction required a relatively slow heat-up period, otherwise aqueous pyrolytic liquefaction takes place. In the semi-continuous unit, the feed enters the reactor and very quickly reaches the reaction temperature of 350°C. Thus rapid pyrolysis rather than catalytic liquefaction occurs, and under these circumstances the presence of the nickel carbonate (catalyst precursor) is deleterious.

Since rapid pyrolysis is now of more interest, one would like to use the unit for rapid pyrolysis studies, but unfortunately the CSTR design results in relatively long residence times for the feed. Whereas this is not a problem in the catalytic liquefaction, it is a problem for aqueous pyrolytic liquefaction where extended residence times lower the yield. As a result, oil yields from this unit are around 20%, whereas with short residence times the yields should be 50-60%.

(b) The second and most important major development is that liquefaction by rapid aqueous pyrolysis has been extended successfully from powdered wood to wood sticks (7.5 cm long and 6 mm square cross section). The physical breakdown of the wood has been characterised, and several parameters of the reaction have been examined. The chemical composition of the oils as a function of some parameters has also been investigated.

(c) As part of a collaborative program, chemical characterisation of the oils from liquefaction studies together with products from upgrading studies has continued in the Department of Chemistry, University of Toronto (Kallury et al. 1983).

(d) Upgrading experiments have been performed on the deoxygenation of phenols (Chow). Although residence times are relatively long, a BASF catalyst (15% Mo_0O_3, 3% NiO_2 on alumina) has proved very effective in producing relatively high yields of benzene without excessive saturation of aromatic rings.

SEMI-CONTINUOUS UNIT

A schematic diagram of the unit is shown in Figure 1. As part of the 1982/83 ENFOR contract the diameter

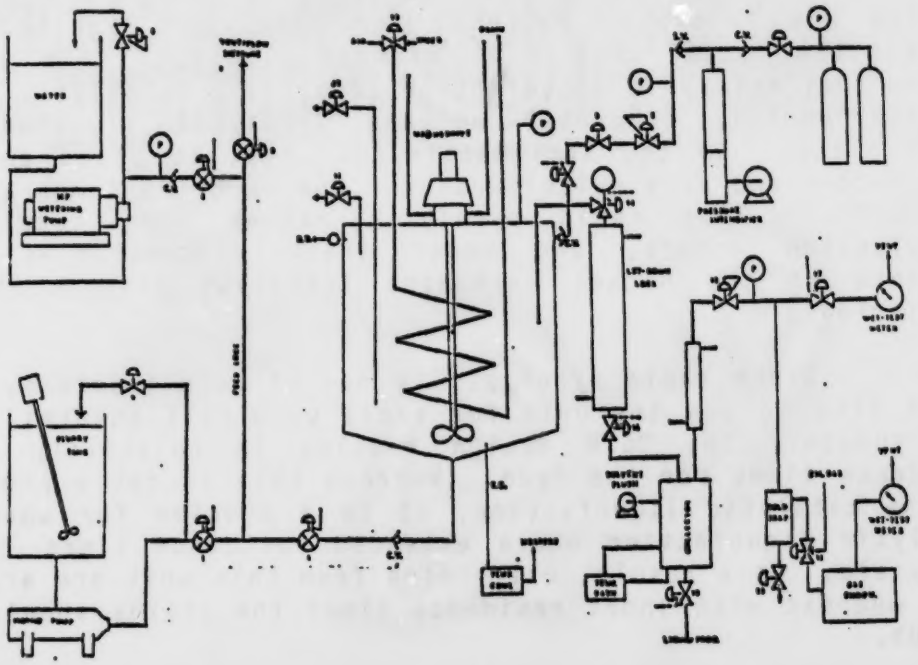

FIGURE 1. Schematic Diagram of Semi-Continuous Unit.

of the feed port at the base of the actoclave was increased, such that the feed line could be attached to the autoclave using one simple adaptor. Previously a more complicated fitting resulted in a constriction in the feed line and plugging was a problem. Several runs were made during which various problems were encountered and rectified. The general operation involved the use of water/wood/nickel carbonate slurries in ratios of 10:1:0.2. No plugging problems were encountered with these concentrations so long as wood of less than 0.42 mm mesh size (< 60 mesh) was used. In the range 0.42 mm to 0.63 mm (60-40 mesh), plugging occasionally occurred. The vertical feed lock (325 ml) was filled from the recirculating line, and, by appropriate valve operation, the slurry was forced along the feed line by high pressure water. The feed rate was higher than had been anticipated when the unit was designed, so that settling problems in the lock could be avoided. This coupled with a thermal shock and resulting leak problem at the inlet fitting precluded feeding of the total lock content to the autoclave. Also, because of possible settling problems, it was considered wise to recharge the lock before making a subsequent feed.

The major mechanical problems encoutered in the operation of the unit occurred between the feed valve 4 and the reactor inlet. In an earlier run using the 40 to 60 mesh wood, the seat on the downstream side of valve 4 deformed when a wood particle jammed behind it. Later, when the thermal shock problem was identified at the inlet fitting, the feed line was lagged. This caused overheating at valve 4, and the dowstream seat deteriorated. the eventual system which was adopted had lagging and a heater on the inlet fitting, and a cooling coil on the downstream side of valve 4. The thermal shock problem at the inlet fitting was a major limiting factor. It was found that if the temperature of the <u>outer</u> surface of the lagged fitting dropped more than 10°C below the reactor temperature, the fitting usually leaked. One potential solution to the problem is to feed more <u>continuously</u> and more slowly. However, with slow feeding we believe that settling of the slurry, both in the lock and feed line, would be a problem.

Two runs have been carried out for the IEA program using the DN 38 poplar. The first used nickel carbonate, but, since it was apparent that rapid aqueous pyrolysis was occurring, the second run excluded the catalyst precursor and hydrogen.

Results are presented here for the first run. Tables 1, 2, and 3 give information on analytic data for the feed and products, element and mass balances, and gas yield

Table 1. IEA Test Run April, 14, 1983.

The reactor was charged as follows:

WOOD TYPE: Poplar Clone DN-38 (less than 60 mesh)
CATALYST: Nickel Carbonate
WOOD:WATER MASS RATIO: 1:10
WOOD:CATALYST RATIO: 5:1
TOTAL RUN TIME: 8h 10m.

Components	Mass (g)	[a] % H_2O	[b] % C	[b] % H	% O	[b] % N	[b] % ash
Wood Feed < 60 mesh	1000	5.65	46.20 [c] 49.20	5.86 [c] 5.80	[d] 47.32 [c] 45.10	-	0.62
Nickel Carbonate Feed	250						
Wood and Nickel Carbonate Recovered	563	11.5					
Char	80	-	9.46				
Oil [e]	112	7.2	69.59	6.98	[d] 21.81 15.27 (maf)	0.39	1.62
Aqueous Phase Organics (Ether Extractable)	48		63.59	7.03			no ash
Gas (see separate table)							

a Moisture content determined by this laboratory (Karl-Fischer and oven drying) unless otherwise indicated.
b Analysis on undried sample by Schwarzkopf Microanalytical unless otherwise indicated.
c Moisture and ash free
d By difference - includes moisture oxygen.
e Phase separated plus acetone solubles.

Table 2. Mass and Element Balances for IEA Run

Carbon

Input (g C)		Output (g C)	
Wood	440	Oil	78
$NiCO_3$	17	Gas	114
		Recovered Wood	193
		Recovered $NiCO_3$	8
		Aqueous Phase	
		Organics	30
		Char	8
	457		431 (94.3% of Feed)

Mass Balance (Ex H_2O)

Input	Mass (g)	Output	Mass (g)
Wood (maf)	944	Oil (maf)	104
Nickel Carbonate	250	Char	80
Hydrogen	5	Gas	310
	1199	Recovered Wood	414
		Recovered Nickel Carbonate	83
		Aqueous Phase Organics	47
	(86.7% of Input)		1038

Oxygen Balance (Ex H_2O and $NiCO_3$)

Input	Mass oxygen (g)	Output	(mass oxygen g)
Wood	433	Oil	17
		Recovered Wood	190
		CO_2 other than from $NiCO_3$	197
		Aqueous Organics	15
		(96.7% of feed)	419

Table 3. Gas Production and Composition for IEA Run

Gas Composition (Volume %)

Component	Discharged During Run (91 L) 1	2	3	4	5	6	From Autoclave(101 L) 7a	7b
CO_2	92.4	91.2	93.0	92.2	93.0	91.6	74.9	68.7
CH_4	4.8	6.1	5.2	6.1	5.4	6.4	20.3	26.6
C_2H_6	0.87	1.1	0.87	0.83	0.86	1.0	2.8	3.0
C_2H_4	8.0×10^{-3}	5.0×10^{-3}	2.0×10^{-3}	NIL	NIL	NIL	NIL	NIL
C_3H_8	1.6	1.3	0.84	0.72	0.70	1.4	1.95	1.7
C_3H_6	0.44	0.22	0.06	0.14	NIL	NIL	NIL	NIL
CO	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL

Gas Products Weights

Component	During Run* (g)	From Autoclave** (g)
CO_2	165	142
CH_4	3.7	17.0
C_2H_6	1.1	3.9
C_2H_4	0	—
C_3H_8	1.9	3.6
C_3H_6	0.3	—

*Obtained using average gas composition for samples 1-6
**Obtained using average gas composition for samples 7a + 7b

and composition data. The extended residence time results in considerable gasification over and above that resulting from pyrolysis of the nickel carbonate. By analogy with results of experiments in our tubular reactor, we believe that the nickel carbonate is pyrolysed to yield nickel oxide and carbon dioxide, and that the former is resistant to reduction to nickel metal. Allowing for this, it is calculated that 46% of the wood carbon is gasified, 39% appearing as carbon dioxide. The oil yield (20%) is correspondingly low as compared to 50-60% in the tubular reactors without nickel carbonate and 35% with the catalyst precursor.

It is impossible to obtain water balances, since high pressure water is inevitably mixed with feed slurry. Our approach was to calculate a carbon balance first and then a mass balance, neglecting water. It was hoped that a deficiency in the mass balance would exhibit itself as an oxygen deficiency in the oxygen balance (ex. water and nickel carbonate). In tubular batch reactors, the water yield was about 14% based on the wood. If the same water yield occurs in the semi-continuous runs, the 70-80 g of water produced would go a long way toward improving the mass balance (from 86.7% to about 93%) but would yield a positive oxygen balance. However, we suspect that the oxygen balance is the least reliable of those calculated, since it ignores both water and nickel carbonate.

The second IEA run was terminated after 4½ hours when (as found later) the liquid level in the reactor fell below the level of the dip-tube. There is no level indicator in the reactor, but we now know that a sudden increase in the volume of gas discharged is due to liquid level falling too low. This second run did show that in the absence of nickel carbonate and hydrogen, gas production from the wood is diminished.

Extensive renovations surrounding the facility have recently taken place, and the equipment is being reassembled for further runs. In an effort to reduce the residence time, the dip-tube and stirrer have been lowered as far as possible. Future runs will be run in a fast pyrolysis mode.

LIQUEFACTION BY RAPID AQUEOUS PYROLYSIS

(Porretta, Holysh, Agblevor)

The most important development over the last year has been the discovery that poplar wood pieces can be

liquefied by rapid aqueous pyrolysis. These studies are carried out using small tubular batch reactors (10 mL) heated in a fluidised sand bed. Data can be collected quite rapidly using this system. The results from individual tubes run under identical conditions are highly reproduceable. The tubes are equipped with thermocouples, and a gas handling device has been designed to measure the volume of gas produced and its composition. Good mass and element balances can be obtained, although the water product is measured using a second tube. The standard pieces studied were 7.5 cm long and had a 6 mm square cross section. Although these pieces liquefied when heated to 350°C over a period of 3 minutes, the heat-up could be as long as 11 minutes without significant decrease in yield. Contrary to our previous experience and statements, even when the sticks were brought to 350°C over a period of 1 hour in an autoclave 15% of acetone solubles were produced.

Process parameters which have been investigated include heating rate, wood/water ratios, final temperature and wood size. Product parameters measured include oil yield, char yield, gas production, aqueous organics and chemical constituents of the oil. Some of the more important results are shown in Figures 2 and 4.

Figure 2 shows the dried products, but this is somewhat deceptive as the wood takes up water and swells before breaking down and producing oil. The two highest temperature samples flow when heated slightly.

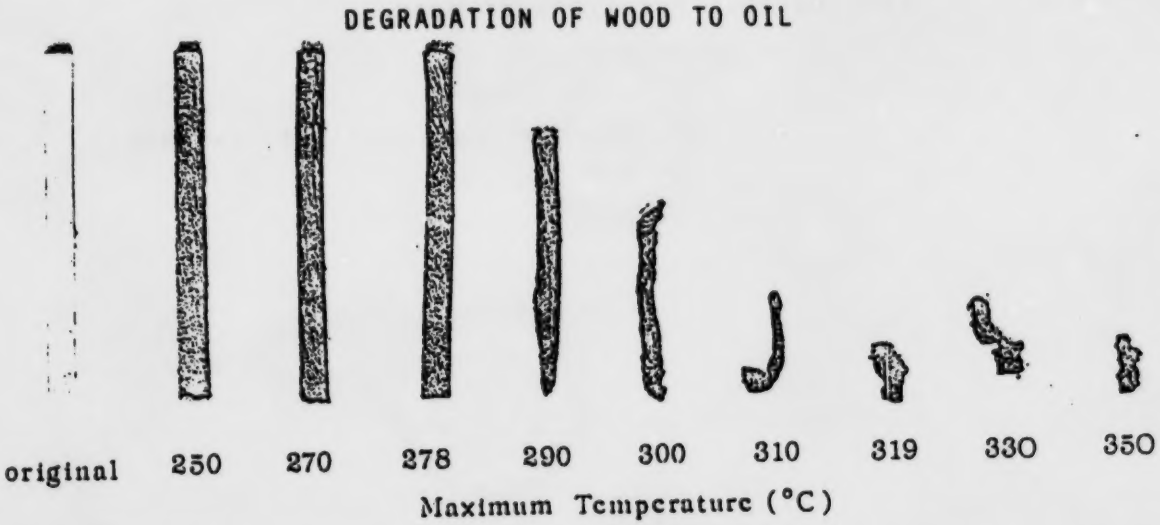

FIGURE 2: Fast Aqueous Pyrolysis of Wood

Figure 3 shows acetone insolubles, acetone solubles and ether solubles as a function of temperature, the same heating rate being used in all cases. At 350°C the acetone solubles are produced in a 50% yield while the ether solubles

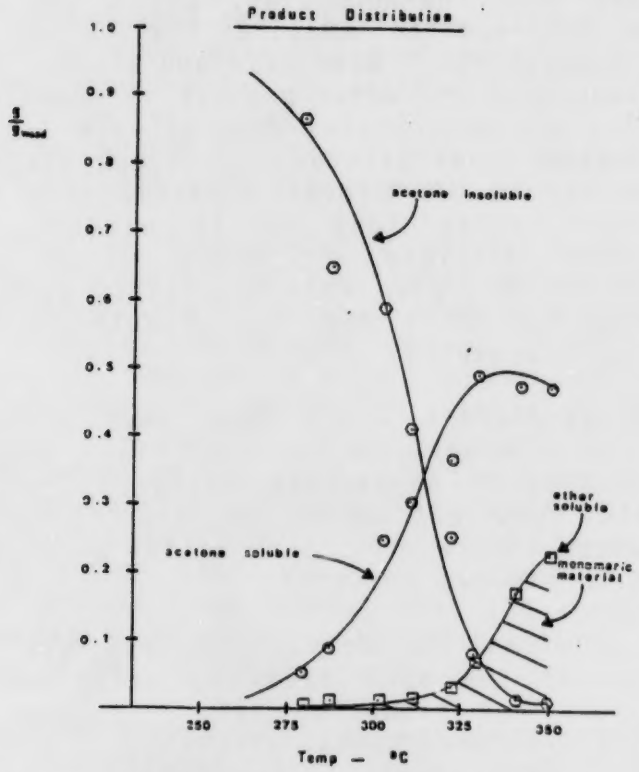

FIGURE 3: Fast Aqueous Pyrolysis of Wood

are approximately 25%. Figure 4 shows oil yield curves for different water/wood ratios. In these experiments the amount of wood is kept constant and the amount of water varied. This results in slightly different heating curves for each ratio. The slowest heating rate (as measured by the thermocouple in the tube) is for the lowest water/wood ratio of 1:1. At this ratio most of the water is quickly absorbed into the wood, and this slows heat transfer to the thermocouple and presumably to the wood also.

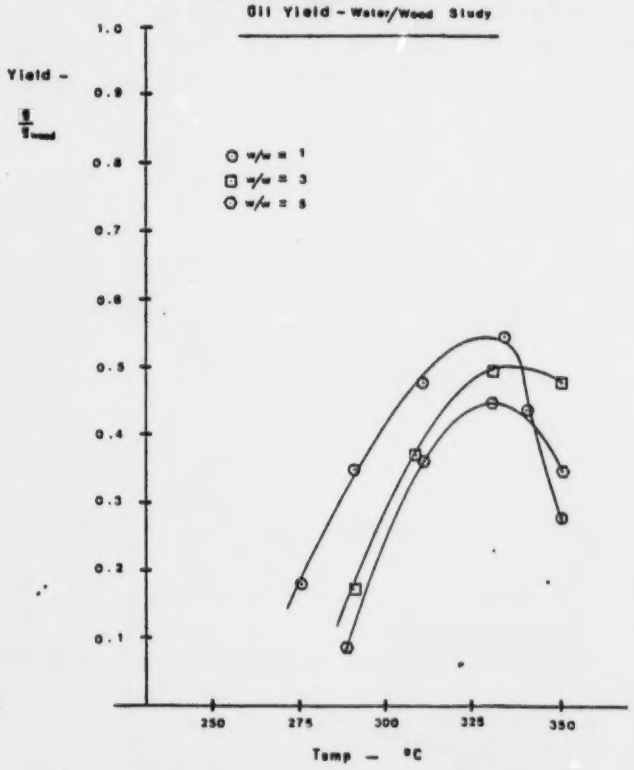

FIGURE 4: Fast Aqueous Pyrolysis of Wood

Figure 5 shows the yields of phenol, alkyldimethoxyphenols, dimethoxyphenol, guaiacol and catechol as a function of temperature. Both phenol and the alkyldimethoxyphenol are the major phenols produced up to 340°C, but beyond this phenol continues to be produced, and the alkyldimethoxyphenols disappear rapidly. Interestingly the phenolics (at 350°C) make up 50% of this fraction. Since the ether solubles mass yield is 25% from the wood, the overall mass yield of phenol is an impressive 6%. Our results on rapid cellulose liquefaction show that little, if any, phenol is produced from pure cellulose. If this result can be extended to the wood, then the mass yield of phenol from lignin is at least 25%.

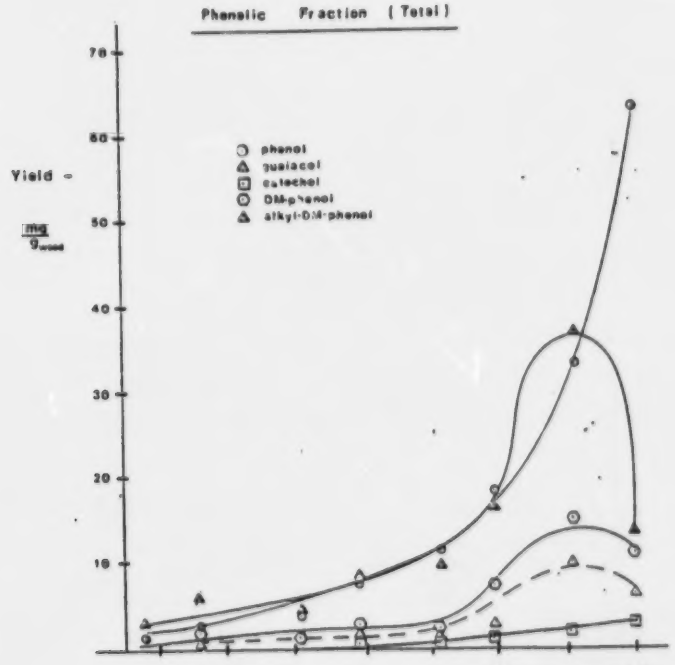

FIGURE 5: Fast Aqueous Pyrolysis of Wood

Elemental analysis of the oils show that the initially formed oils contain 25-30% oxygen.

As a result of the high yields of phenol, we have initiated studies on lignin isolated from steam exploded

aspen. We have also done considerable work on microcrystalline cellulose. Figure 6 shows that conversion of cellulose occurs at a lower temperature than the wood and the products also have lower molecular weights. The formation of individual chemicals has also been monitored.

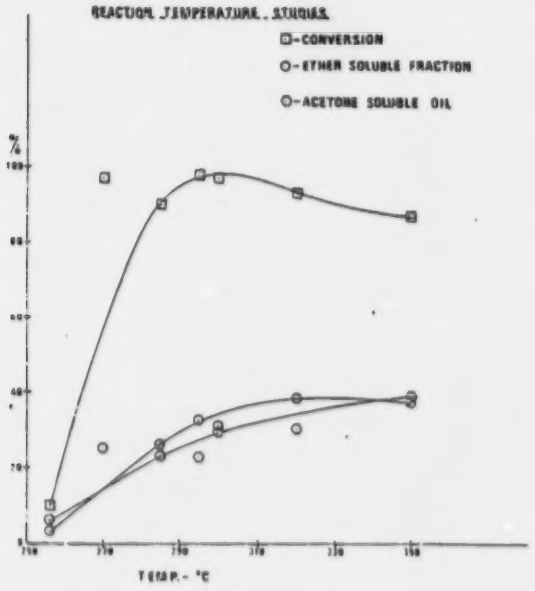

FIGURE 6: Fast Aqueous Pyrolysis of Cellulose

For example, Figure 7 shows the variation in yield of the initial major product, 5-hydroxymethylfurfural.

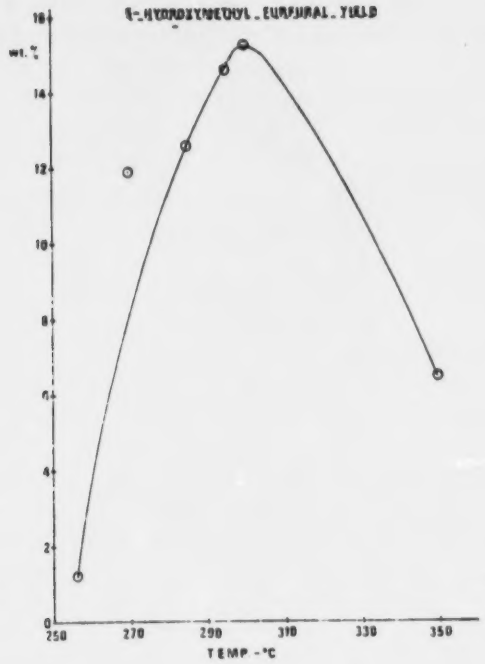

FIGURE 7: Fast Aqueous Pyrolysis of Cellulose

UPGRADING EXPERIMENTS (Chow)

In the last year we have commenced some upgrading experiments. Since phenolics (and particularly phenol itself) are major components of the oil, we have investigated the deoxygenation of phenol with the objective of producing benzene and aromatics without the production of large amounts of saturated products. We were hopeful that we could make use of our rapid heat-up unit and thus obtain some kinetic data. Unfortunately the hydrogen pressures which are required are too high for the tubular reactors, and so our results have been obtained in a 1-L stirred autoclave equipped with a catalyst basket.

Figure 8 shows results for a BASF catalyst which is 15% MoO_3 and 3% NiO_2 on alumina. The autoclave reaches temperature just after 1 hour so most of the reaction is isothermal allowing the possibility for development of kinetics. The three major products are benzene (60%), cyclohexane (20%), and methylcyclopentane (13%). At higher catalyst concentrations (25%) a benzene yield of 68% has been

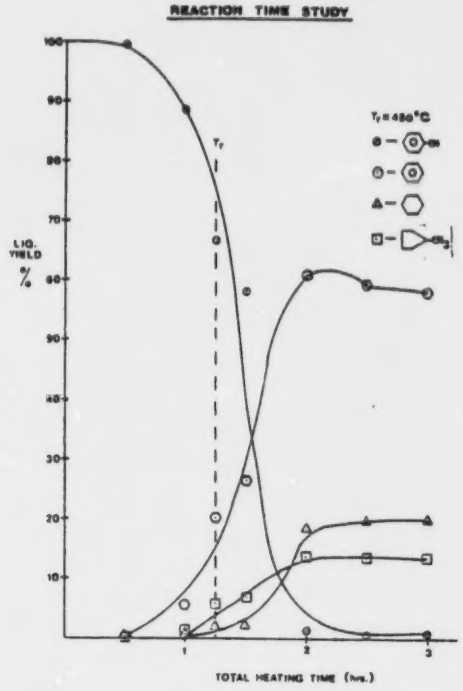

FIGURE 8: Upgrading of Phenol

obtained (see Figure 9). The mechanism for the production of cyclohexane and methylcyclopentane has also been investigated by using cyclohexane, cyclohexene, cyclohexanone and

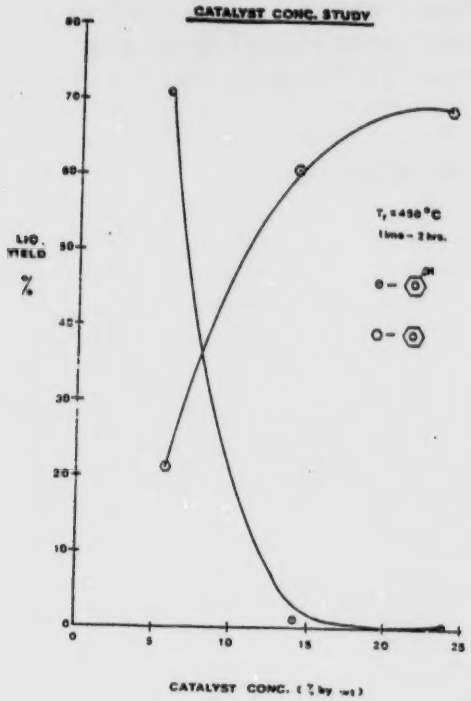

FIGURE 9. Upgrading of Phenol

cyclohexenol as substrates. Figure 8 shows that prolonging the reaction out beyond the time when all the phenol is consumed does not change the ratio of the products, and thus the routes to the three products diverge early in the reaction or are substantially different. Thus cyclohexane is not formed by the hydrogenation of benzene, and cyclohexane and methylcyclopentane are not interconverted by isomerisation. The role of water in deactivating the catalyst is also being investigated.

Work is continuing on phenol together with simple diphenols, methoxyphenols, and alkyl phenols.

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"LIQUEFACTION OF POPLAR: THE UDS PROCESS DEVELOPMENT UNIT AND INITIAL PRODUCT CHARACTERIZATION

E. Chornet[1], R.P. Overend [2], D. Eugène, M. Heitz[3], and M. Rubio[4].

Département de génie chimique
Faculté des sciences appliquées
Université de Sherbrooke
Sherbrooke, Québec, Canada J1K 2R1

(1) to whom all correspondance should be addressed

(2) also affiliated to the National Research Council of Canada

(3) also affiliated to the Cantre Technique Forestier Tropical, Paris

(4) en congé sabbatique, Universidad de Murcia, Spain

INTRODUCTION

The objectives of our wood liquefaction program are three-fold:

(a) to convert lignocellulosics into a "liquid oil" which can be either blended with conventional crudes or fractionated followed by upgrading of the different fractions;

(b) to conduct the conversion at conditions under which high initial solids concentrations can be processed;

(c) to learn about the sequence of chemical events taking place during liquefaction and in so doing devise appropriate equipment or consider alternate process options to integral liquefaction.

Our initial work, conducted in batch autoclaves, led to the now well accepted conclusion that biomass materials are extremely reactive and can be transformed (or converted) at less drastic conditions than those used for coal using short reaction times of the order of minutes.

Based on the initial work, largely unpublished, we designed a cascade system by means of which we could separate the preheating stage from the liquefaction stage. We expected to learn precise information about the initial stages of liquefaction and the interplay between macromolecular desaggregation, solvolysis and pyrolysis. The cascade work was extremely useful in three main areas:

(i) it showed that mechano-chemical effects could be used advantageously to desaggregate (defibrate) the cell wall structure of lignocellulosics and moreover they could lead to some defibrilation which will facilitate solvent penetration leading to solubilization. This had an important process application insofar we could envision the preparation of concentrated suspensions (slurries) having between 20 and 30% (by weight) wood derived material. Such concentrations are to be achieved by rapid defibration of diluted suspensions followed by successive additions of new material;

(ii) the use of a "carrier oil" results in lower operating pressure conditions than with water;

(iii) the "carrier oil" could eventually be chosen to induce solvolytic action. A recycle cut will be the ultimate choice. The solubility parameters to be optimized are unknown at present but guidelines could be obtained from the extensive literature work on lignin and cellulose solvents.

Based on the former considerations a continuous process development unit (PDU) was designed in the summer/fall 1981. The equipment procurement was conducted between winter/summer 1982 with construction and commissioning lasting through the winter 1983. Design modifications together with operational runs have been conducted since May 1983. In what follows we will describe the components of the PDU, the design parameters and the operational data obtained through the summer 1983 in connection with the IEA testing program.

BASIC CONCEPTS IN WOOD LIQUEFACTION

Liquefaction of lignocellulosics is aimed to achieve "solubilization" of the different macromolecular structures present in wood (or, generally speaking, biomass). These macromolecules belong to four different families: hemicelluloses, lignin, cellulose and extractives. The architectural arrangement of the four families and more precisely of the three main families (extractives are at low concentrations in boreal hardwoods) makes it very difficult to treat thermochemical reactions as being identical (or similar) to the reactions of more simple molecules. We are thus initially in the presence of high-order systems possessing a definite three-dimensional arrangement having a fibrous character.

Any attempt to liquefy biomass must consider defibration as an initial and essential step needed to break down the ultrastructure of wood. Mechano-chemical effects (caused for instance by sudden decompression) and solvolytic action (breaking down the weak links present in wall-to-wall bonding) can facilitate defibration. Individual fibers are composed of a microfibrilar arrangement held together by strong adhesion and/or bonding through lignin or direct H-bonds between the cellulosic chains. A second important step in liquefaction will consist in defibrilation yielding a very disperse colloidal-type system of microfibrils in a solvent media. Whether this defibrilation can be completely achieved is not important at this point of the discussion. What matters is the possible separation of the smaller entities, the microfibrils, prior to its depolymerization into polysaccharide structures which should rearrange themselves in the solvent like a micellar system. The depolymerization cannot probably be accomplished by mechanical means only.

Temperature and/or chemical interaction (solvolysis or catalysis) are most likely needed to facilitate depolymerization. In fact, temperature alone suffices to decompose wood (pyrolysis) into smaller chemical entities resulting from dehydration, functional rearrangements, and C-C and C-O bond breaking. The difference between pyrolysis and depolymerization is simple: pyrolysis refers to "random scissions" whereas depolymerization could be defined as "order-like scission".

Once defibration and defibrilation are accomplished the "integral liquefaction route" will follow a pyrolytic approach in the presence of a solvent which can interact in the stabilization of free-radicals produced by thermal excitation. Alternately, depolymerization can be attempted after defibrilation. This leads to a fractional liquefaction route which essentially separates wood into two primary products: a hemicellulose-rich fraction containing some lignin derivatives and a cellulose-rich fraction with the remainder of the lignin. The extent of lignin in either fraction will depend essentially on the choice of solvent used and on the thermo-mechano-chemical device used to effect the fractionation.

In our ongoing integral liquefaction program we have thus followed a two-step approach:

(1) A solvolytic-defibration-defibrilation step aimed at achieving progressive enrivhment of wood-derived material by successive additions of freshly ground wood. The precise goal is to achieve 25% weight wood material in the slurry to be liquefied;

(2) A liquefaction reactor in which the concentrated slurry is rapidly processed at temperatures in which pyrolytic reactions are dominant. This reactor acts essentially as a "solubilizer" although it can also work as a true "wet-pyrolyzer" or "cracker" if the temperature is raised to higher levels.

DESCRIPTION OF THE P.D.U.

A schematic representation of the PDU is presented Figure 1. A 10 ℓ holding reservoir is initially filled with 6 to 8 ℓ of a wood/creosote oil suspension containing 14-20% weight of wood (<0.3 mm). The suspension is agitated and heated to temperatures up to 240°C. This final preheating temperature has not yet been fixed and range comprised between 160-240°C is so far been investigated. The point to be made is that in order to achieve "good pumpability" and "sufficient degradation" the macromolecular structures we felt that the cellulose had to be heated near its glass transition temperature that the defibrilation, during rapid recirculation, is conducted in the plastic state thus facilitating breakd of the microfibrilar network through repeated passages across the defibrilation valve.

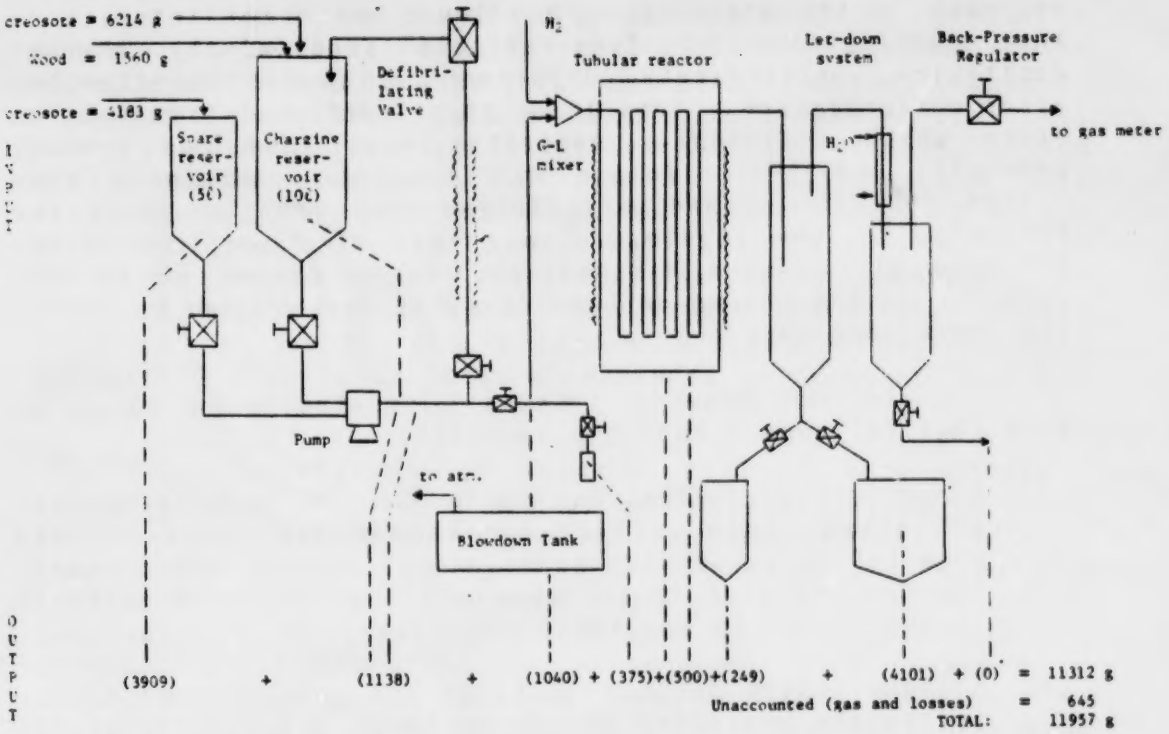


FIGURE 1. Schematic of UDS process development unit Numbers correspond to experiment LB-005 Wood used is IEA - Populus Deltoides.

The linear velocity during the recirculation-defibrilation step is kept between 1.0 and 1.4 m/s. The differential pressure across the defibrilating valve can be varied within wide ranges but it is generally comprised between 13.8 and 20.8 MPa. In all our experimentation a minimum of three passages through the valve was used to ensure "uniform degradation" of the lignocellulosic materials. This criterion was based in earlier quantitative microscopic analysis of the sheared material.

During recirculation-defibrilation in the creosote oil a significant fraction of the wood material is solubilized. In fact, the hemicelluloses and lignin can be easily scavanged out and solubilized if the preheater temperature is maintained at 240°C. At the same time important morphological changes occur in the cellulose. Its quantification is not yet established although the microscopic examination permits the above affirmations.

Since the initial suspension becomes diluted by the effect of solubilization as described above, additional amounts of wood can be introduced to raise the "wood material concentration" up to 30% weight of the overall suspension. A viscous slurry is thus prepared and ready to be sent to the liquefaction section of the PDU.

The liquefaction section is comprised of a tubular reactor maintained at constant temperature via a molten salt bath. The reported experiments were conducted with a reactor having a 17.0 m length and 0.48 cm as internal diameter. Typical slurry velocities during liquefaction were comprised between 0.3 and 0.8 m/s. Liquefaction temperature was maintained at 315-325°C and it is quickly reached by the slurry in the initial 3 m of the tubular reactor.

The liquefaction has been conducted so far in a H_2 reducing atmosphere. The gas and slurry are mixed prior to entering the tubular reactor. A specially designed jet-mixer is used. The G/L ratios are comprised between 2-24 ℓ_{STP}/ℓ_{SLURRY}. The liquefaction is conducted at pressures of about 7.0 MPa.

Following liquefaction two high pressure reservoirs are used to separate slurry and gas. A back pressure regulator allows decompression of the gas and its measurement via a test meter. On-line samples allow trapping of the gas phase for further analysis. The high pressure reservoirs are equipped with automatic valving systems to facilitate transfer of the processed slurry to atmospheric pressure containers.

At the end of a particular run pure solvent from a spare reservoir is flushed through the system to recover any solid material that could have sedimented inside the tubular reactor.

EXPERIMENTAL

A summary of a series of 8 runs is reported herein.

The first three runs were made to assess the operational capabitilies of the system. Two objectives were pursued:

(a) to study the pumpability patterns using progressive enrichment and defibrilation at low-to-intermediate temperatures (160-240°C). The conditions used have been defined in the section describing the PDU;

(b) liquefaction of concentrated slurries having about 25% weight of wood-derived material. Low temperatures (315-325°C) and pressures (5.5-10.3 MPa) were used during these runs;

Runs 4 through 8 had as objectives:

(c) to obtain significant amounts (a few liters) of wood-derived oils;
(d) conduct overall material balances;
(e) assess eventual operational problems.

The operation of the PDU has been satisfactory once the understanding of the defibrilation valve was achieved. This required two different design configuration:

Due to the need to maintain the slurry in rapid movement (otherwise settling and plugging does occur) residence times in the liquefaction reactor were very low (21-57 s). In order to increase the conversion and liquid yield we kept the slurry in the liquefaction reactor for a period of about 5 min by interrupting the pumping action. As it will be shown later this experiment (LB-007) resulted in high conversions and liquid yields and suggested the installation of a longer reactor (89.5 m with 0.6 cm I.D.).

During runs 1 through 8 the gas analysis was not properly made due to difficulties in defining a precise data sampling point within the short residence times used in the initial reactor configuration.

RESULTS AND DISCUSSION

A complete material balance is presented in Figure 1. It corresponds to run LB-005.

Material balances	Based on slurry (wood + creosote)	Based on slurry + spare reservoir
input	7774 g	11957 g
output	7129 g	11312 g
unaccounted for	645 g	645 g
% closure	$\frac{7129}{7774} \times 100 = 91.7\%$	$\frac{11312}{11957} \times 100 = 94.6\%$

The following remarks lead to corrections which improve the material balances:

* the slurry is considered to be the wood + creosote being processed;

* the slurry + spare reservoir is the overall material initially prepared in the two reservoirs (spare + charging);

* the wood had an initial moisture content of about 10% by weight of the material;

* gas analysis corresponding to run LB-007 proved that CO_2 formation can be estimated at 10% weight of dry wood. If we apply this percentage to run LB-005 we should consider 140 g of CO_2 as being formed;

* pyrolytic H_2O is not measured. Based on our own experimentation we estimate a 10% weight production of H_2O from dry wood at 320°C;

* the corrected material balances are (in g):

H_2O present as moisture = 156
H_2O from pyrolysis = 140
CO_2 from pyrolysis = 140
losses = 209
645

$$\% \text{ closure} = \frac{7774-209}{7774} \times 100 = 97.3\%$$

Analysis of the data

The product slurry poured and filtered very easily with most of the oils found in the filtrate. Only a few percentages are found in the THF extraction of the residual solids obtained as filter cake.

In order to understand the extend of liquefaction our analysis involves product slurry at three different stages of liquefaction. The data combines experiments 007 and 005.

Product slurry after preheating - defibrilation at 230°C

* THF insolubles = 9.4% weight of total slurry:

* total unconverted (THF-insolubles) solids found in product

  $\{(6214 + 1560) - 645\} \times 0.094 = 670.1;$

* total conversion

  $1 - \frac{670.1}{1560 - 156} = 0.52$ (Note that 156 g is the moisture in the thrtral wood)

* "oil" yield estimate

  $0.52 - \frac{1}{2}\frac{(140 + 140)}{1560 - 156} = 0.42$

  Note that this "oil yield" is uncertain since H_2O and CO_2 from pyrolysis will appear between 200 and 325°C. We estimate that half of the pyrolytic H_2O and CO_2 has been given off at 230°C.

Product slurry after liquefaction at 325°C (residence time ~ 30 sec)

* THF insoluble = 6.1% weight of total slurry;

* total unconverted (THF-insolubles) solids found in product

$\{(6214 + 1560) - 645\} \times 0.061 = 434.8$ g;

* total conversion

$$1 - \frac{434.8}{1560 - 156} = 0.69$$

(Note that 156 g is the moisture in the initial wood)

* "oil" yield estimate

$$0.69 - \frac{(140 + 140)}{1560 - 156} = 0.49$$

Product slurry after liquefaction at 325°C (residence time ~ 5 min)

* THF insolubles = 2.3% weight of total slurry

* total unconverted (THF-insolubles) solids found in product;

$\{(6214 + 1560) - 645\} \times 0.023 = 164.0$ g

* total conversion

$$1 - \frac{164.0}{1560 - 156} = 0.88$$

* "oil" yield estimate

$$0.88 - \frac{(140 + 140)}{1560 - 156} = 0.68$$

"Oil" characteristics

Elemental analysis of the oils is presented in Table 1. Defibrilation does not result in significant deoxygenation as compared to the lower O content shown by the products from liquefaction. Calculation have been made by taking into account the data concerning oil yields and arithmetic average of the overall O content.

Table 1. Elemental analysis of liquid "oils" derived from liquefaction of Populus Deltoides in Creosote oil

Sample	% N	% C	% H	% O	% O in wood derived "oil"
initial creosote	1.2	90.6	6.6	1.6	n.a.
following defibrilation at 230°C (no. 008-001)	1.3	86.7	5.5	5.5	33.4
following liquefaction at 325°C for ~ 30 s (no. 007-finished)	1.1	88.0	6.6	4.3	20.8
following liquefaction at 325°C for ~ 5 min (no. 007-5 min)	1.2	86.8	5.5	5.5	22.7

Distillation characteristics of the oils produced are presented in Table 2. Significant amounts of light materials are rapidly obtained even during the defibrilation step. These light products are probably carcked during liquefaction at very short residence times and more light product is formed with extended liquefaction (~ 5 min). Also, solubilization of the cellulosic fraction proceeds via formation of soluble large fragments with subsequent cracking during extended liquefaction.

TABLE 2 Distillation cuts (% weight) of liquid oils derived from liquefaction of Populus Deltoides in Creosote Oil (Temperatures in °C)

Sample	IBP<T<205	205<T<345	345<T<407	T > 407
initial creosote	1.1 (-)	91.4 (-)	-	7.5 (-)
following defibrilation at 230°C (no. 008-001)	3.5 (20.7)	88.1 (64.5)	-	8.4 (14.8)
following liquefaction at 325°C for ~ 30 s (no. 007-finished)	2.4 (10.4)	85.4 (48.6)	-	12.2 (41.0)
following liquefaction at 325°C for ~ 5 min (no. 007-5 min)	4.0 (16.8)	88.0 (73.0)	-	8.0 (10.2)

Note: Numbers in parenthesis indicate percentages of the different fractions related to wood-derived oil only. Calculations were made using the arithmetic means of the reported oil yields

Characterization of residual solids

The determination of particular chemical characteristics and morphology of the unconverted material can facilitate the comprehension of the interplay between defibrilation, depolymerization, solvolysis and pyrolysis.

Table 3 shows the elemental analysis of the unconverted solids. The pretreated and defibrilated material has an elemental composition similar to that of cellulose (C:44.4%; O:49.3%; H:6.2%) but with some deoxygenation, probably due to decarboxylation, which increase the C content of the residue relative to O. With rapid liquefaction at 325°C (~ 30 s) some dehydration and probably more decarboxylation take place resulting in increased C content. With extended liquefaction (~ 5 min) the augmentation of the C content of the residue suggest initiation of the charring process which essentially consists of recondensation of free-radicals formed during dehydration and deoxygenation. No explanation has been attempted to account for the observed increase in nitrogen content of the solids.

TABLE 3 Elemental analysis (% weight) of unconverted residual solids derived from liquefaction of Populus Deltoides in Creosote Oil

Sample	N	C	H	O by diff	ash
initial wood (anhydrous)	0.1	44.5	5.2	49.8	0.4
following defibrilation at 230°C (no. 008-001)	0.4	48.2	6.0	44.6	0.8
following liquefaction at 325°C for ~ 30 s (no. 007-finished)	0.5	49.3	5.7	43.2	1.3
following liquefaction at 325°C for ~ 5 min (no. 007-5 min)	1.2	57.2	4.8	33.5	3.3

Note that the inorganic matter is included in the O-by difference calculation

Analysis of the solid residue was also investigated by a combination of T.G./D.T.G. following a methodology developed in our analytical laboratories. The analysis revealed that the liquefaction unconverted residue contained negligeable lignin (or lignin-derived polymers). The analysis also showed that the cellulosic component has been significantly changed since the thermal decomposition peak measured via the T.G./D.T.G. technique shifts to lower temperatures probably suggesting a structural change to either less rigid (less crystalline) or different polymeric sub-structures due to the extensive dehydration and de-oxygenation.

In order to further explore these structural changes we conducted a series of morphological studies on the residue via scanning electron microscope. This analysis yielded the following information:

* the solid residue resulting from the preheating and defibrilation step shows almost total defibration and extensive defibrilation (peeling off patterns in Illustration 008-002);

* the solid residue from rapid liquefaction (~ 30 s) shows increased external solvolytic action on the defibrilated fragments. The cellulosic fragments seem to have undergone a melting stage but the solvolytic action does not appear uniform (Illustration 005-008);

* the solid residue from extended liquefaction (~ 5 min) shows very thorough solvolytic action. Moreover the residue appears as a solidified material obtained from a melted polymer (cellulose?). Formation of char is also encountered in some fragments of the residue (Illustration 007-5 min).

CONCLUSION

In this presentation we have reviewed the background knowledge that has led to the design and operation of the UdS process development unit for biomass liquefaction in the presence of a carrier oil.

The technology proposed in this paper consists of a preheating stage (at 160-230°C) in which, by rapid recirculation and decompression of a wood-oil slurry across a specially designed "shear device", extensive defibration and initial defibrilation takes place together with

solubilization of the hemicelluloses and most of the lignin. By successive additions of ground wood concentrations up to 30% of wood-derived material in the slurry can be achieved.

The liquefaction stage is conducted in a tubular reactor operating, in the present experiments, at about 325°C. Short residence times in the reactor (~ 30 s) did result in poor conversions (~ 69%). Longer residence times (~ 5 min) increased conversion up to about 88% with "oil" yields of about 68%. Hydrogen is used to prevent unwanted oxidations during liquefaction. Overall pressures have been maintained between 5.5 and 10.3 MPa for these experiments.

Our results have given clear evidence of the important role of the initial preheating stage on the overall solubilization. The liquefaction stage involves mainly cellulose conversion and the interplay between solvolysis and pyrolysis must eventually dictate the course of the defibrilation, depolymerization and cracking reactions. Within the limited experimentation so far conducted we are not able to focus on the mechanisms involved and their importance during the overall liquefaction process.

ACKNOWLEDGMENTS

The authors are indebted to the National Research Council and to the Natural Sciences and Engineering Research Council of Canada for financial support of this project.

The contributions of J. Khorami, G. Chauvette and H. Mênard to the analytical aspects of this project are gratefully acknowledged.

The microscopy studies were made possible through a grant from the Ministry of Education of Quebec through its F.C.A.C. program.

(a)

(b)

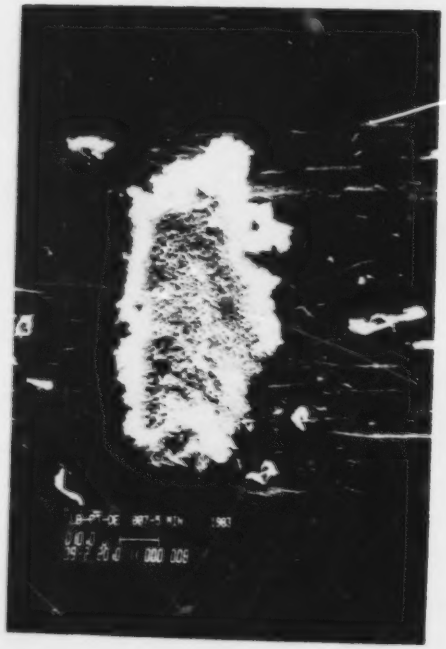
Illustration 008-002 - Solid residue following preheating at 230°C and defibrilation through sudden decompression of Populus Deltoides in creosote oil. Photograph (b) shows an enlargement of the tip of the fragment illustrated in (a).

(a)

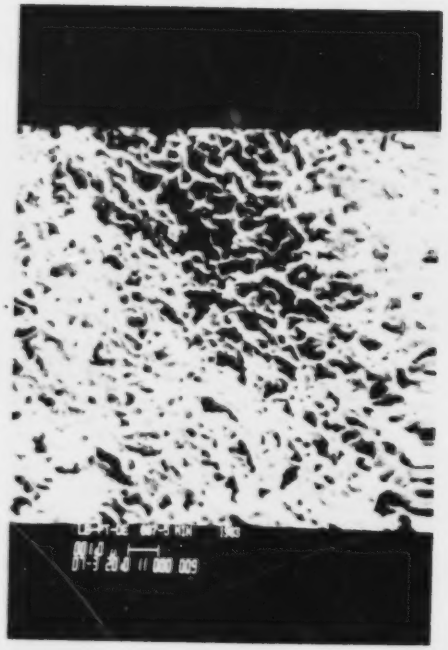
(b)

(c)

Illustration 005-008 - Solid residue following rapid liquefaction at 325°C (∿ 30 s) of Populus Deltoides in Creosote Oil. (a) and (b) show hollow fibers with solvolytic action exposing the microfibrilar characteristics. A "melting" effect seems to have occurred in the high shear areas of the residue. (c) shows a three-fiber aggregation still retaining some of the original configuration but in highly disordered state.



(a)



(b)

(c)

Illustration 007-5 min - Solid residue following rapid liquefaction at 325°C (∿ 5 min) of Populus Deltoides in Creosote Oil. (a) shows a general detail of the extensive solvolytic action; (b) is a blow-out of central portion of (a). Note the "new structure" probably resulting from resolidification of the melted cellulose; (c) shows the formation of char together with some ill-defined cellulosic material.

THE RIT HIGH PRESSURE DIRECT LIQUEFACTION EXPERIENCE.

A. Bergström, A. Kannel and C. Sylwan

Department of Chemical Technology
Royal Institute of Technology
Stockholm, Sweden

INTRODUCTION

At the last Specialists Meeting on Biomass Liquefaction, 1982, Pehr Björnbom mentioned (1982) the continuous bench scale equipment. Since then it has been completed and has been working quite successfully. About 20 runs have been performed making a total of 120 hours runtime. the raw material has mostly been peat. Figure 1 shows a schematic drawing of the unit.

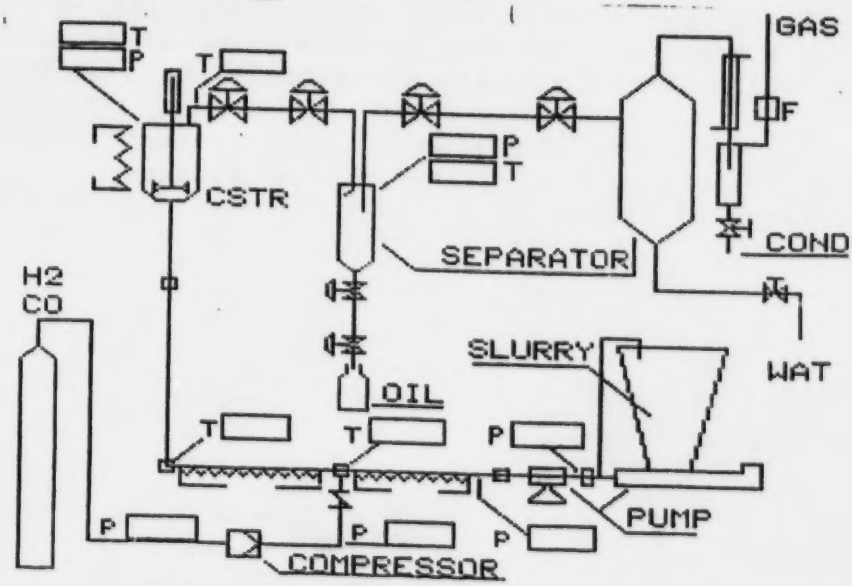


FIGURE 1. Oil from Peat and Biomass LDU Unit

The raw peat having 15-20% dry substance is passed through a meat mincer to cut the fibres. The slurry is prepared in the funnel to 10-14% dry substance. It is pumped around and homogenized by a Moyno-pump and then fed into the

high pressure system by a Burdosa plunger pump. The plunger pump is followed by two tubular pre-heaters leading into the bottom of a 5 litre continuous stirred tank reactor. The stirring is accomplished by a magnedrive stirrer from Andreas Hofer Hochdrucktechnik GmbH. In the last runs the separator vessel has been by-passed. The product is let out through two stem and seat valves and sent to a water-cooled receiver at atmospheric pressure. From the receiver the product is tapped into buckets. A system for feeding solid material directly into the reactor is also being developed.

For technical data of the equipment see Appendix 1.

PROCESS CONTROL

The schematic flow sheet of the unit (Figure 1) was produced by a computer. It is a Swedish Luxor micro-computer called ABC-800. It is connected to the continuous unit.

During a run the display will indicate the flow sheet with current values in respective squares. Control system is shown in Figure 2.

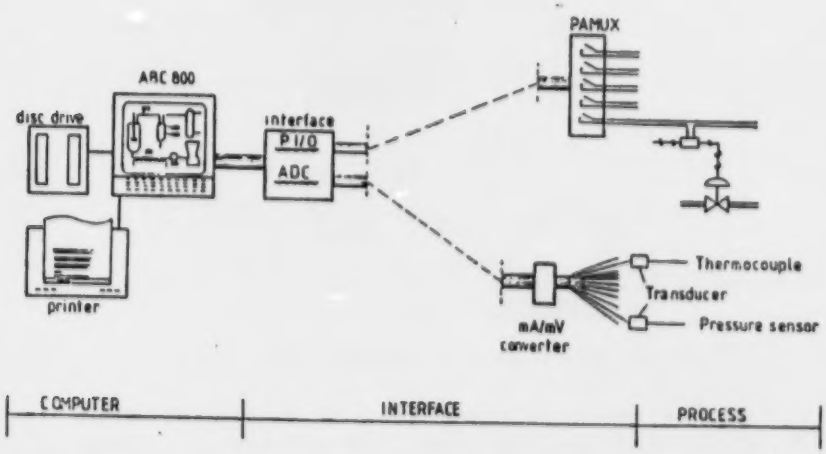


FIGURE 2. LDU Process Control

The measuring device gives the current value as an analog signal. That signal is converted into corresponding digital value by the ADC-card (Anaglog-Digital-Converter).

To this ADC-card 16 analog instruments can be connected. The set point value for the reactor pressure can be changed during a run. When the pressure reaches or exceeds that value a pressure let down sequence will be initiated by the program. The signal goes from the computer to an input/output interface between the computer and a parallel addressable multiplexer (PAMUX). That is a circuit board on which 16 industrial power I/O relays can be placed. The valves are directly connected to these relays. Up to 64 PAMUX boards can be connected to the computer. The control/measure loop is repeated every second and once every minute the computer collects valuable data and stores it on a disc and prints it.

HIGH PRESSURE SOLIDS FEEDER

The solids feeder Figure 3 feeds directly into the reactor through a connection in the reactor lid. It is activated hydraulically and can feed peat and biomass against a pressure of 30 MPa (Björnbom et al 1983). The dry peat concentration should be about 25%.

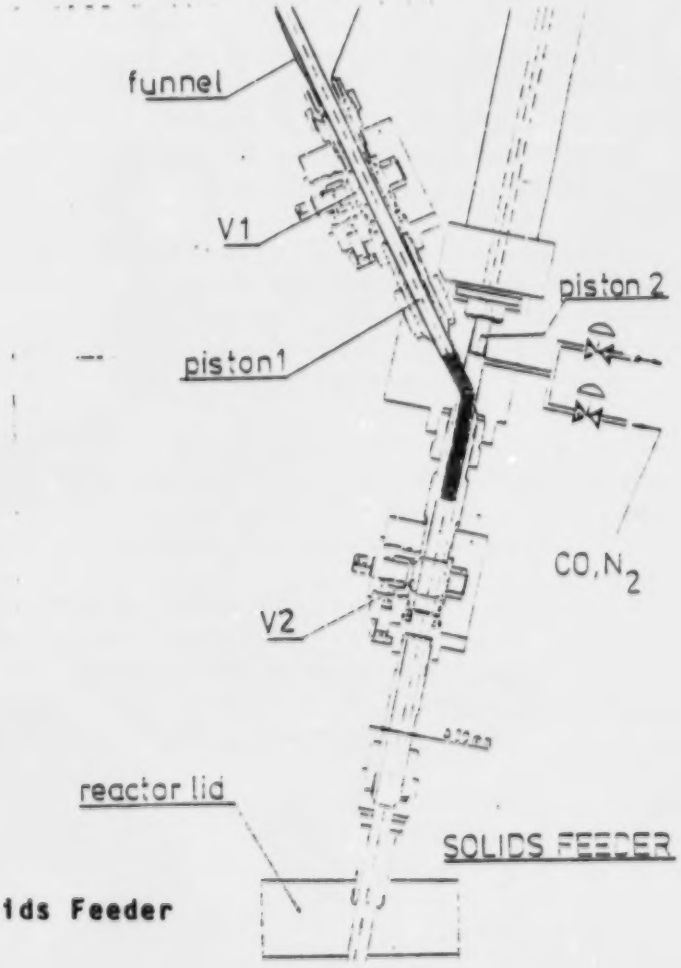


FIGURE 3. Solids Feeder

V1 and V2 are loaded on two tubes, the latter leading into the reactor. V1 and V2 are two hydraulic ball valves, piston 1 is pneumatically activated and piston 2 is activated hydraulically.

A typical cycle is as follows:

Valve 2 is in closed position and piston 2 is in its upper position. Piston 1 feeds peat from the funnel through valve 1 which is open. On the lower end of piston 1 there is mounted a metal spring which makes it possible to push the peat past the two tube joint and into the vertical pipe. Piston 1 feeds 10 times, then it stops at its upper position and valve 1 closes. Gas is now pumped into the space between the two ball valves by the lower pipe in the Figure. This last step prevents steam, evolving from the reactor, from condensing inside the solids feeder and thereby raising its temperature. When the gas pressure amounts to approximately the same value as the pressure inside the reactor vessel, valve 2 is opened and the substance is pushed into the reactor by the hydraulic piston 2. The piston goes up again and stops just above valve 2 which will close. The space between valve 1 and 2 is depressurized to prevent blowing out the dry substance in the funnel when valve 1 is opened. Piston 2 is taken to its top position before valve 1 is opened and the cycle starts again.

The solids feeder is connected to the computer and the cycle is controlled by the program. Mechanical switches are mounted on the solids feeder for position control of pistons and ball-valves preventing collisions or reactor blow out.

SLURRY PUMP

The slurry is fed into the high pressure system by a piston pump with electric motordrive Figure 4. It is a standard pump with rather big check-valves. The ball diameter is 11 mm.

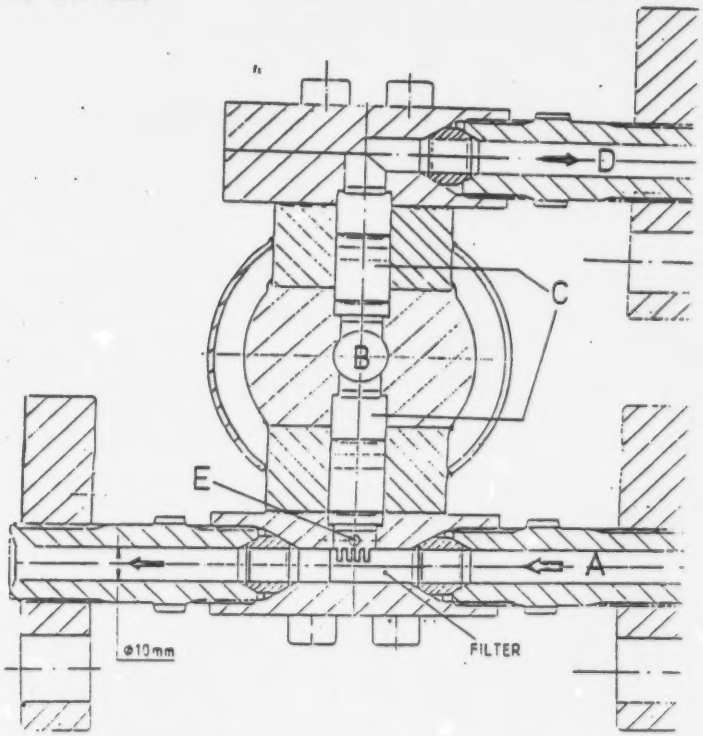


FIGURE 4. Slurry Pump Cross Section.

The slurry enters at 'A' directly from the Moyno pump. 'B' is the piston and 'C' are two check-valves. A certain amount of the slurry is pumped into the preheaters and the rest recirculates to the slurry tank.

To prevent sand particles from getting stuck into the valves an extra metallic filter have been put in. If sand particles of > 1 mm enters the pump, the check balls will be blocked. The filter is a cylindrical stainless steel pipe (9/10 mm) with four 1 mm broad slits.

If the filter is plugged it can be backflushed with a liquid pulse through 'E'.

In Figure 5 can be seen the PI-unit that indicates on the screen if there is a pressure fall before the pump meaning that the filter is blocked. If so valve 1 can be opened from outside by the solenoid 'S'. 'E' is the same flush water inlet from another view.

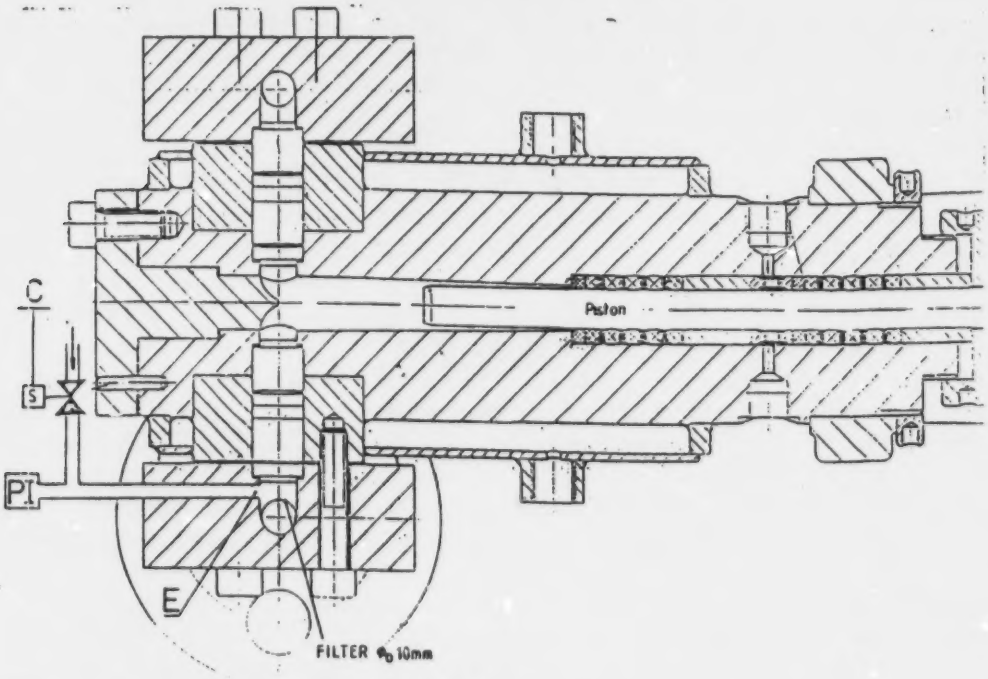


FIGURE 5. Slurry Pump Axial Section.

PREHEATERS

The preheaters consist of two stainless steel pipes (9/14 mm) wound with Termocoax heating elements. the elements consist of a resistance wire enclosed in a metal sheath, and insulated from the sheath by compacted magnesium-oxide powder. The power is 1500 W per meter tubing.

REACTOR

The reactor is a 5 litre backmixing reactor with magnedrive stirring. Because of the high dry substance the peat most hold when fed with the solids feeder it would be impossible to pump it through a tubular reactor. During the residence time of 30 min the peat reacts and becomes pumpable. The reactor is electrically heated, controlled by a PID-anti reset temperature regulator.

VALVES

The outlet valves are two stem and seat valves. The product from the reactor is a four phase system, consisting of gas, oil, water and solid residue and we had the idea that regulating valves would have problems. The valves work one at a time in a lock sequence over a pressure drop from reactor pressure to atmospheric pressure.

RECEIVER

The liquid product and the gas is separated in the receiver at atmospheric pressure and 90°C. The gas goes to a gas meter, the liquid is let out and weighed.

RESULTS

Table 1 shows some experimental and analytical results (Hörnell et al 1983) from our runs. The tendency is for more of the product to be soluble in THF when the run is made at higher temperature. The mean molecular weight, by GPC, of what is soluble seems to decrease with increasing reaction temperature. The product also sediments easier the higher the reaction temperature.

TABLE 1

EXPERIMENTAL RESULTS

Raw material: Finnish peat having 11-14% dry material
Reaction time approximately 30 min

EXP.	P/MPa	temp/C	% THF soluble of dry product	Mean molecular weight by GPC (PS, 310 nm)
13	10.0	300	53	1350
14	10.0	300	52	1400
15	8.0	280	44	1500
16	13.0	320	60	1200
17	10.0	300	51	1450

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APPENDIX 1

Technical data

Burdosa plunger pump

Slurry rate	l/h	0 - 12
Working pressure	kp/cm^2	0 - 523
Piston diameter	mm	9
Stroke volume	cm^3	0 - 3.2
Stroke length	mm	0 - 50
Piston force	kp	360

Preheaters

1 meter tubes 9/14 mm wound with:

Heating elements: Thermocoax from SODERN, France, diam 1.5 mm

Power per meter tubing	W/m	1500
Material in resistance wire	80/20 NiCr	
Insultant in resistance wire	Magnesium oxide powder	
Sheath material	Stainless steel	

Reactor

Material	Stainless steel 5 NiCrTi 2615	
Temperature	°C	-10 - +550
Volume	l	5
Pressure	MPa	30/35
Temperature	°C	500/350
Electric heating	kW	5
Voltage	V	220

Agitator

Permanent magnet rotary agitator (stuffing box free)

Working pressure	MPa	350
Output torque	Ncm	300
Maximum speed	r/min	3000

Drive: Direct current motor, directly flanged-on via V-belt pulley

Valves

Autoclave engineers	9/16 inch air to open		
Maximum temperature	°C	200	
Hydrostatic test	MPa (PSI)	106	(15 450)
Gas test	MPa (PSI)	71	(10 300)

AN UPDATE ON VTT'S DIRECT LIQUEFACTION PROGRAM

P. McKeough and Y. Solantausta

Fuel and Lubricant Research Laboratory
Technical Research Centre of Finland (VTT)
02150 ESPOO 15
Finland

1. AIM

The aim of the current project at our laboratory size is to identify the most favourable process concepts for the direct liquefaction of peat and wood. The ultimate products of interest are transport fuels. The important steps in such processes are:

- pretreatment e.g. drying, grinding
- slurrying and pumping
- primary liquefaction
- separation of primary product from unreacted raw material
- upgrading of primary product into transport fuels

These individual steps are interrelated, for example:

- pretreatment determines slurrying properties
- slurry concentration affects liquefaction capacity
- pretreatment affects reactivity
- liquefaction severity determines possible separation methods and the upgrading requirement.

As a consequence of this high degree of interrelation, it is not possible to optimize the process by optimizing the individual steps. Rather, one must attempt to optimize, as a whole, the entire process from raw material to transport fuel.

Note that another raw material of interest in the current project is the lignohemicellulosic waste from the pulp industry.

2. METHODS

The central method in this research will be economic evaluation. Experimentation will play an important supportive role.

Of the important process steps, the following are to be investigated experimentally:

- pretreatment
- slurrying and pumping
- primary liquefaction

Experimental research of the solids-separation and upgrading steps is beyond the resources of the current project. Two methods for evaluation of these steps will be considered:

1. Application of knowledge obtained in coal liquefaction research. A precondition for use of this method is that the primary liquid product resembles coal liquids which have been succesfully separated and upgraded. This fact was emphasized at the last Review Meeting (McKeough, P. and Solantausta, Y., 1982). Specifically, it was then suggested that a fairly severy primary liquefaction should be employed to produce an oil with a relatively low oxygen content.

2. Application of hypothetical separation and upgrading routes based on analysis of the primary liquids. An example of this method would be application of upgrading data for some pure compound to a group of related compounds in the primary product. The probability of success of this method is, as yet, undetermined.

3. EQUIPMENT

As regards pretreatment, a variety of equipment is available at the Technical Research Centre. This will be (and has been) used to produce different materials for both the slurrying and the liquefaction experiments.

The unit employed in slurrying and pumping studies is depicted in Figure 1. It was designed to simulate the feeding section of conventional high-pressure direct liquefaction processes. The scale of the unit is, however, small, for example, pipe internal diameters of 6 to 10 mm, check valves with balls of 9.5 mm diameter. The high-pressure loop is operated semi-continuously between 5 MPa and 25 MPa.

A hot-charged batch reactor is to be the primary tool for liquefaction research. Since the last Meeting its design has been

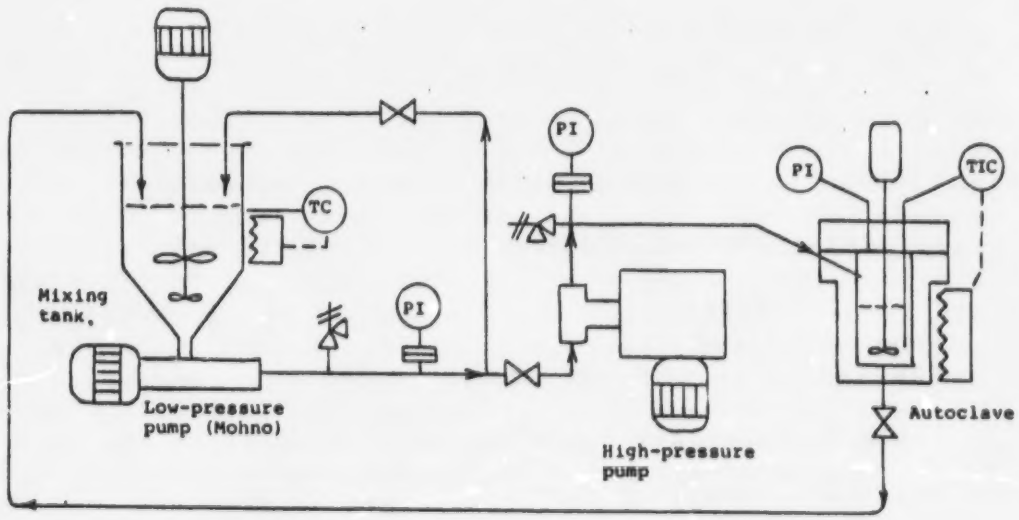


FIGURE 1. Slurry Test Unit

somewhat modified. Figure 2 presents the current configuration. This unit should be able to heat-up a 200 to 300 ml batch of slurry to reaction temperature in less than 5 minutes.

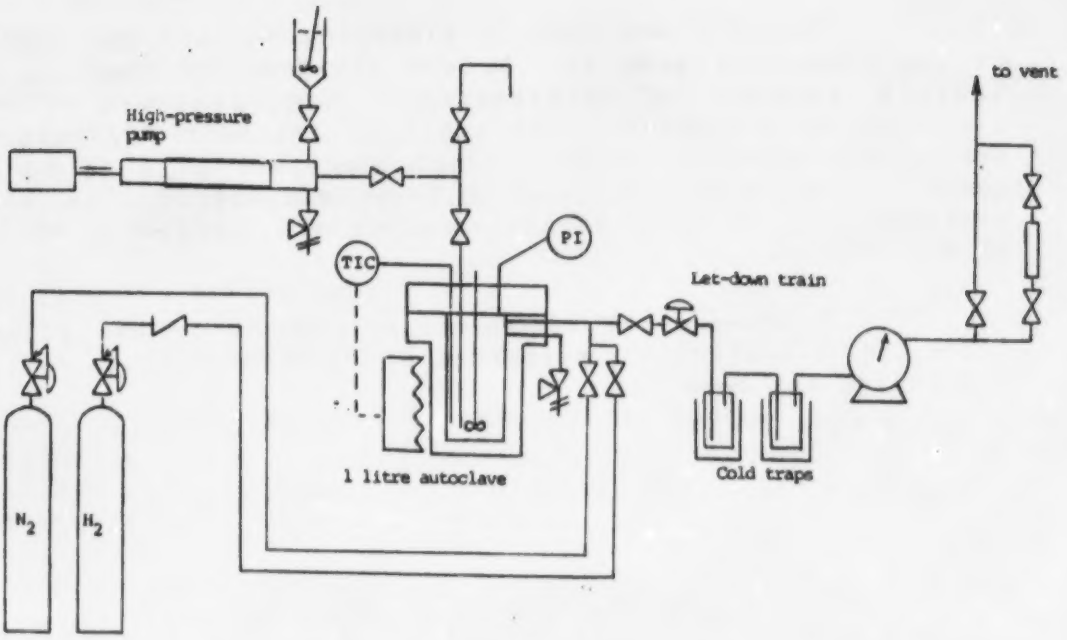


FIGURE 2. Hot Charge Batch Liquefaction Unit

4. EXPERIMENTAL PROGRAM

Table 1 presents a list of the pretreated peat and wood materials that have, so far, been selected for study. The variables are, of course, moisture content and particle

Table 1 Materials to be tested

Material	Preparation	Moisture Content	Particle Size
A	Milled Peat (H5), Ground in Disc Mill	40%	100%<0.5 mm 90%<0.25mm
B	Peat (H5), Dried, Ground in a Ball Mill (15min)	10%	100%<0.5 mm 90%<0.2 mm
C	Peat (H5), Dried, Ground in a Ball Mill (60min)	10%	100%<0.5 mm 90%<0.09mm
D	Wood Chips (Aspen), Dried, Ground in Hammer-Type Mill	10%	100%<0.2 mm
E	Wood Chips (Aspen), Dried, Ground in Hammer-Type Mill	10%	100%<0.4 mm
F*	Wood Chips (Aspen), Ground in a Disc Mill	30-40%	100%<0.5 mm

* Not to Date Prepared

size. A maximum particle size of 0.5 mm was imposed because of the small scale of the slurry unit. However, even in large-scale plants, larger particle sizes have rarely been used. Other criteria used for selection were:

- required prehandling technology to be available
- wide ranges of moisture content and particle size to be covered.

One potential feed material has been omitted from the study: raw peat (containing about 90% moisture). The direct liquefaction of this material is being studied elsewhere (Björnbom, P., 1982).

The objectives of the pretreatment experiments are to verify that the above materials can be produced and to generate data for the determination of equipment sizes and energy requirements.

The objective of the slurrying and pumping tests is to determine, for different slurry mediums, the maximum solids concentrations handable in the experimental unit. Two slurry media have been chosen for the initial slurry experiments: anthracene oil and water. The former simulates a recycle oil of an actual process. The tests with water are performed mainly for reference purposes, because, as discussed later, recycle oil is considered the more promising carrier. (This is another reason for the omission of raw peat as a material to be studied). The method used to determine the maximum solids concentration is as follows.

- A slurry of certain concentration is mixed
- The unit is operated
- If no flow disturbances occur within a certain period of time (typically 1/2 hour), the solids concentration is increased.
- This procedure is continued until the occurrence of flow disturbances.

The objective of the liquefaction tests is to study the liquefaction of the above materials under a variety of conditions. In initial tests, the choice of conditions will be constrained somewhat by findings of earlier literature studies. The most important is the use of recycle oil rather than water as the slurrying medium. In addition, the initial experiments will focus on non-catalytic systems with hydrogen as reducing gas. Reaction conditions such as temperature,

pressure, and heat-up rate will be widely varied. The important dependent variables are oil yield, oil quality, and reducing gas consumption. As the research work proceeds, the experimental conditions will be, to a greater and greater extent, dictated by the outcome of economic evaluations. The objective is not so much to develop a new liquefaction process as it is to identify the most economic overall concept.

5. ACHIEVEMENTS

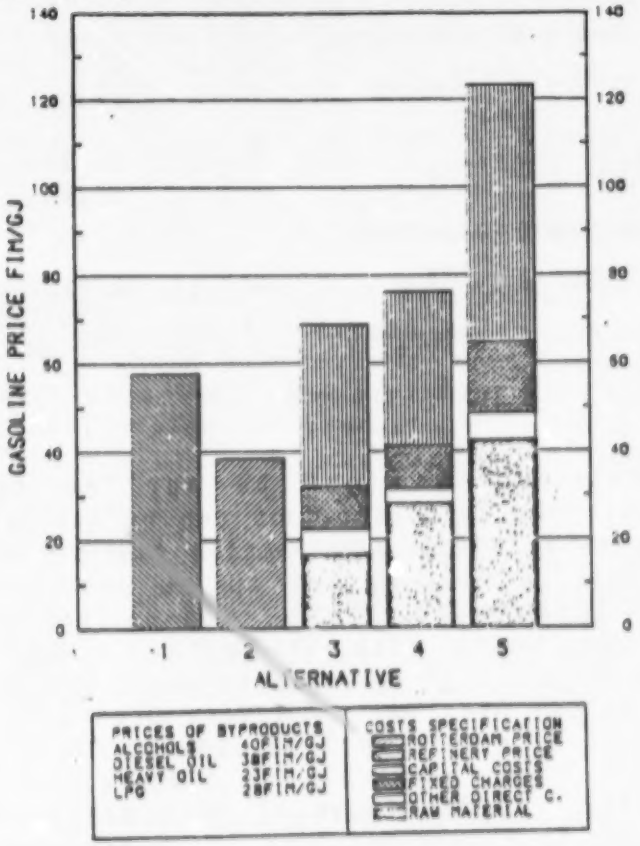
The main accomplishments have been:

- an economic evaluation of a process for the direct liquefaction of peat,
- completion of slurry experiments for four materials.
- an experimental study of alternative methods for recovery and analysis of liquefaction products.

The experimental program on primary liquefaction is somewhat behind schedule. The liquefaction unit is currently being installed and should be ready before the new year.

For the economic evaluation, a coal liquefaction process - the H Coal process - was applied to peat. However, as it turned out, the only significant unknown was the ratio of carbon dioxide yield to water yield (these being the two alternative deoxygenation products). Two different values for this ratio were applied. Another area of significant difference between the coal and the peat cases was pretreatment, but here the required modification was straight forward. In the study, it was also possible to vary, over a limited range, such variables as feed moisture content and

feed reactivity (as affected by pretreatment). Figure 3 presents the results of this economic study. The cost of gasoline produced via direct liquefaction (the best case of the study) is lower than those via indirect liquefaction (Mobil, Fischer-Tropsch), and not very much higher than the Finnish refinery price. Note, however, that capital-related costs are relatively high for the direct liquefaction process, so that its gasoline price is very sensitive to the chosen interest rate (here 10%). The study also indicated that the result is not very sensitive to variations in the feed moisture content (0 to 20%) or in the carbon dioxide/water ratio. (The latter finding is consistent with the results of a separate study comparing deoxygenation routes in liquefaction (McKeough, P., 1983). The result is however, moderately sensitive to variations in feed reactivity.



COLUMNS: 1) AV. REFIN. PRICE OF GASOLINE 1-9/81 2) AV. ROTTERDAM PRICE OF GASOLINE 1-9/81 3) DIRECT LIQ./CONCEPT OP 4) KT/MOBIL 5) KT/FISCHER-TROPSCH

BASIS OF CALCULATION: ANNUITY 10%. SERVICE LIFE 20A. AS OF 1.9.81.

FIGURE 3. Comparison of Prices of Gasoline from Peat and Petroleum

The results of the slurry tests carried out as part of the BLTF comparative test program are presented in Table 2. As far as peat is concerned, the aim of the study has been largely fulfilled. That is, for most of the

Table 2. Results to Date of Slurry Tests

TEST	SLURRY COMPOSITION	TEMPERATURE	MAXIMUM SOLIDS CONCENTRATION (DRY BASIS)
1.	MATERIAL A - WATER	65 C	25%
2.	MATERIAL A - ANTHRACENE OIL	110 C	33%
3.	MATERIAL A - ANTHRACENE OIL	75 C	24%
4.	MATERIAL B - ANTHRACENE OIL	110 C	40%
5.	MATERIAL C - WATER	65 C	24%
6.	MATERIAL C - ANTHRACENE OIL	110 C	43%
7.	MATERIAL D - WATER	65 C	NO SUCCESS AT ANY CONCENTRATION
8.	MATERIAL D - ANTHRACENE OIL	110 C	15%-18%

pretreatments which might be applied to peat, the corresponding feed concentrations can be estimated. This is not so for wood, where quite a lot has still to be done. Firstly, tests 7 and 8 need to be duplicated, although significant change in their outcome is not expected. Secondly, the tests with the other proposed materials (Table 1) are still to be undertaken. At this stage, the wood-water system does not seem very promising, but, before condemning it, an effort will be made to crosscheck with the experience of other workers, for example, in the pulp and paper industry. Other types of mill may produce material more conducive to slurry-handling.

Note that the temperatures selected for the slurry tests were:

- 80°C for water slurries
- 110°C for oil slurries

The former was limited by the requirement to restrict water evaporation, the latter by equipment restraints. Unfortunately, the actual temperature employed in the water tests was somewhat lower - 65°C - as a result of a technical problem. The effect of this temperature difference will be checked in a later experiment. As is evident in Table 2, one anthracene oil test (test 2) was also conducted at a lower temperature (test 3). The reason for this was the high moisture content of the solid material (40%), leading to significant evaporation of water at the higher temperature of 110°C. It should be remembered that the results presented in Table 2 may be conservative side owing to the small scale of the test unit.

The study on product recovery and analysis methods was made because of reports in the literature about errors caused by, for example:

- work-up solvent combining with liquefaction product,
- products being lost during solvent evaporation.

The study substantiated that these errors occurred for certain methods and/or certain solvents. A convenient method, avoiding these errors, was developed. It employs acetone as work-up solvent and minimizes contact between hot acetone and the liquefaction product.

6. FINALLY

The current project has two years to run. In that time, through economic studies, slurry tests, and liquefaction experiments, the identification of the most favourable routes for converting wood and peat to transport fuels should have been accomplished.

REFERENCES

Björnbom, P., (1982), The Swedish liquefaction project. 2nd Biomass Liquefaction Review Meeting, Saskatoon, Canada.

McKeough, P. and Solantausta, Y., (1982) The direct liquefaction of peat and wood - the Finnish program. 2nd Biomass Liquefaction Review Meeting, Saskatoon, Canada.

McKeough, P., (1983), Oxygen removal during the direct liquefaction of low-rank materials. Fuel, 62,4.

HYDROLIQUEFACTION OF TROPICAL WOODS AND OTHER TROPICAL RAW MATERIALS

by

J. DOAT, D. VINCENT AND M. HEITZ
CENTRE TECHNIQUE FORESTIER TROPICAL
DIVISION CELLULOSE-CHIMIE-ENERGIE
45 bis Avenue de la Belle Gabrielle
94130 Nogent sur Marne
France

Liquefaction (aka hydroliquefaction or hydrogenolysis) of biomass consists in making directly by thermochemical route, under pressure, from a solid material, an hydrocarbon compound having a high energetic value. This process is nowadays studied by many laboratories and societies.

The CTFT has chosen to work on hydroliquefaction of tropical woods, with the following conditions:

- solvent : water
- gas : hydrogen
- catalyst : alkali (soda and sodium carbonate)

1. The first tests were carried out on a reforestration species planted in the Congo on which the influence of the parameters of reaction were determined.

   1.1 Characteristics of the wood: The wood was a selected hybrid Eucalypt : Eucalyptus Tereticornis X Saligna
   - density (bonedry) : 0.57 g/cm^3
   - high calorific value (p.c.s) : 19,830 kJ/kg (or 4,750 Kcal/Kg)
   - elementary composition:
     C : 49.43% H : 6.02% O : 44.0%
   - chemical composition:
     Alcohol-benzene extractives : 2.6%
     Hot water extractives : 1.4%
     Lignin : 29.8%
     Pentosans : 16.5%
     Cellulose : 44.0%
     Ashe : 0.5%

The wood was used in sawdust (granulation between 0.40 and 0.16 mm).

1.2 Characteristics of the apparatus (see Figure 1)

Its consists in:

a) a reactor: volume : 400 ml
max. temp. : 800°C
max. pressure : 50 MPa.
with a magnetic stirrer

b) control and regulation systems

c) a compressor (used if high pressures are necessary)

d) measurement systems for temperature and pressure

1.3 Study of the parameters of the reaction

We studied:

- temperature of reaction
- initial pressure
- pH
- Fype of catalyst, reducing gas and solvent
- yields in oil and tars
- % of residues
- characteristics of both oil and tars
- energetic yields

1.4 Results obtained:

The main results are shown in the graphs and tables

- graphs A for pH (NaOH) and B for Na_2CO_3
- graphs C for time reaction
- graphs D for pressure
- graphs E for volume of solvents
- graphs F for temperature

1.5 Best conditions for treatment

With water and hydrogen, the best results seem to be found for:

- dilution : 100 g/L
- initial pressure of hydrogen : 3 MPa
- Reaction temperature : 300°C
- Time : 30 minutes
- catalyst : Na_2CO_3
- final pH : 4.5 to 5 (NaOH (4%) or Na_2CO_3 (5.3%) or 14% $Na_2CO_3.10H_2O$)

With these conditions, the yield in tars and oils will reach about 40% of the weight of the wood.

And the energetic yield will be not very far from 60%.

II. <u>The second part</u> of the work is now being carried out. We are trying to determine the influence of the nature of the raw materials by applying, the above defined process on well know materials.

These materials are: (see Table G)

- pure cellulose (cotton)
- lignin (prepared by Klason method)
- sugar cane
- different tropical woods (with high lignin content, high extractive content, high carbohydrate content)

The higher the (lignin + extractives) = graphs H

- the higher the yield in oil
- the higher the residue
- the higher the final pH

September 1983

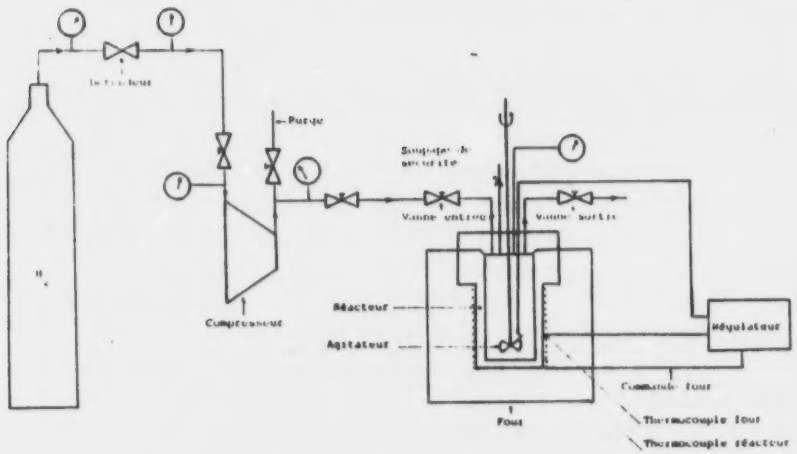
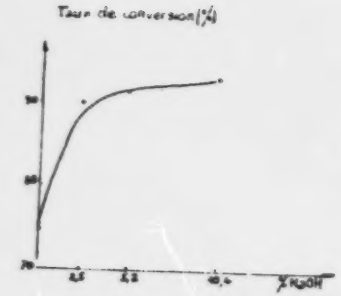


Fig 1 : L'INSTALLATION D'HYDRO-LIQUEFACTION

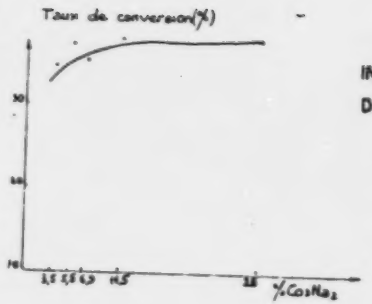
FIGURE 1. L'installation D'Hydro-Liquefaction



(A)

INFLUENCE DE LA QUANTITÉ DE PRODUIT ALCALIN ($NaOH$)

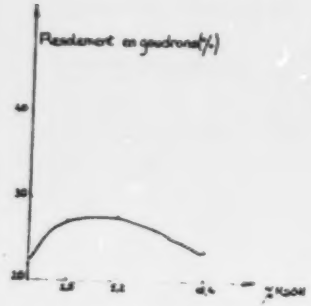
(T=300 °C ; 5 h ; pression initiale = 30 bars)

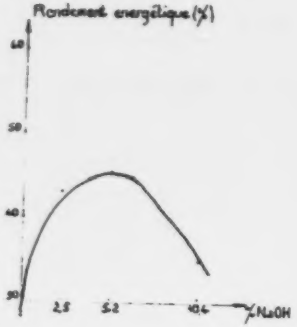


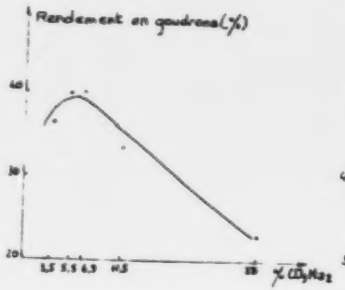
(B)

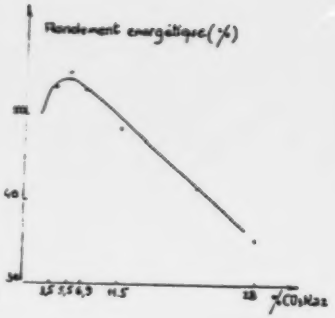
INFLUENCE DE LA QUANTITÉ DE PRODUIT ALCALIN (Na_2CO_3)

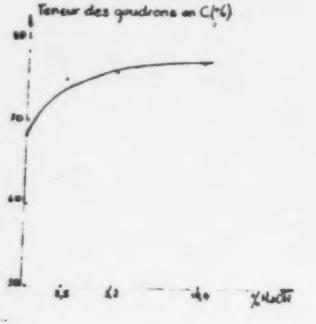
(T= 300 °C ; 1/2 h ; pression initiale : 30 bars)

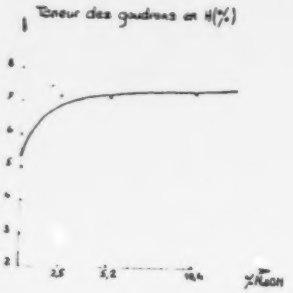


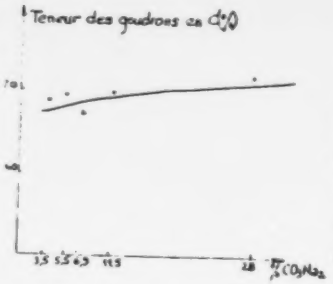


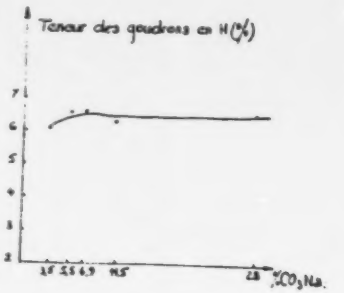


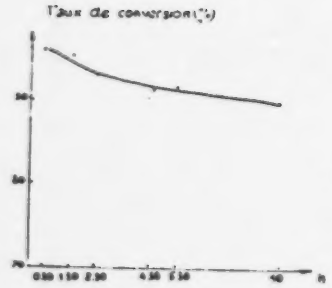






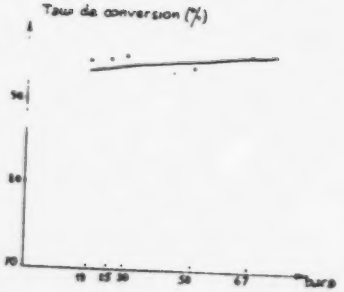






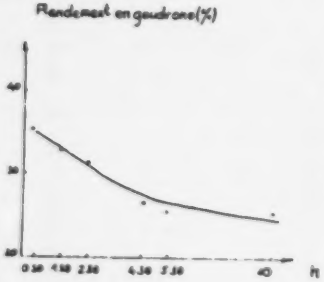
INFLUENCE DE LA DURÉE ⑤
DE RÉACTION

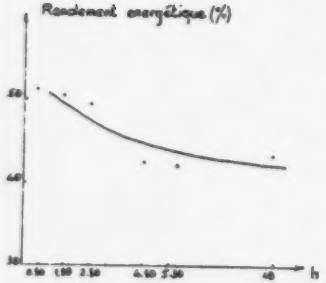
(NaOH = 5 % ; T = 300 °C ;
pression initiale = 50 bars)

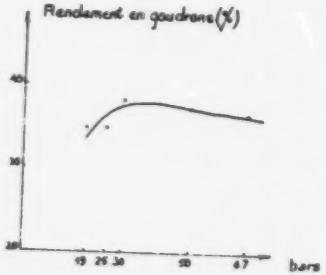


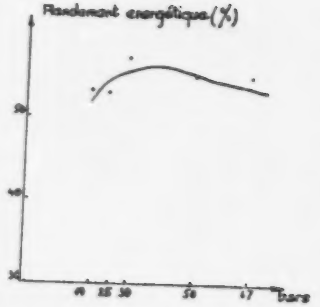
INFLUENCE ⑥
DE LA PRESSION INITIALE

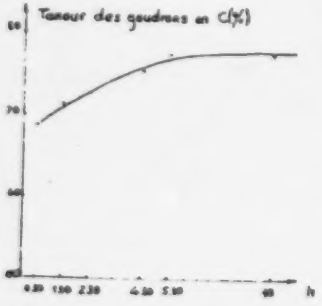
(Na_2CO_3 = 5,3 % ; T = 300 °C ; ½ h

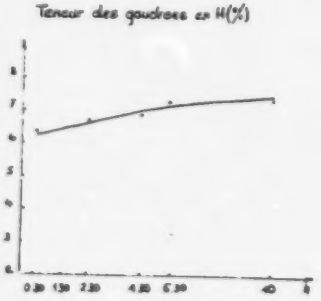


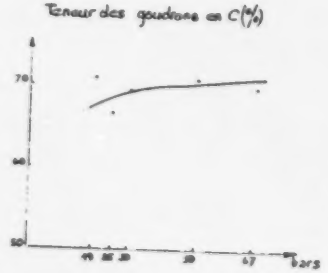


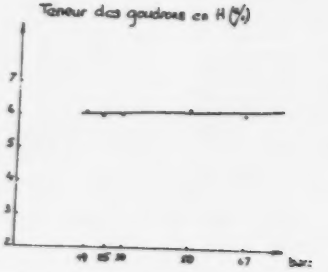










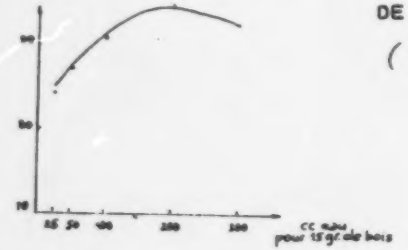


(E)

INFLUENCE DE LA QUANTITÉ DE SOLVANT (EAU)

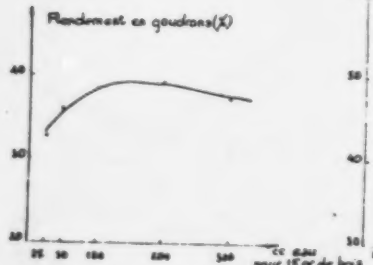
(Na_2CO_3 = 5,2 %, T = 300 °C ; pression initiale = 30 bars)

Taux de conversion (%)



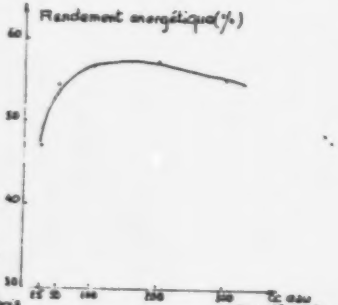
cc eau pour 15 gr de bois

Rendement en goudrons (%)



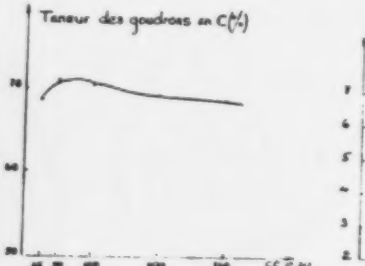
cc eau pour 15 gr de bois

Rendement énergétique (%)



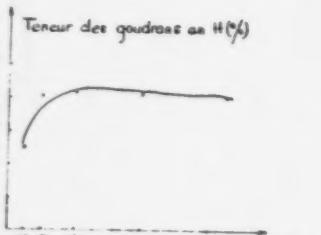
cc eau pour 15 gr de bois

Teneur des goudrons en C (%)



cc eau pour 15 gr de bois

Teneur des goudrons en H (%)



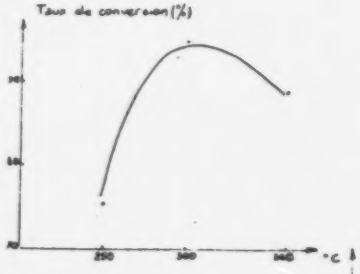
cc eau pour 15 gr de bois

(F)

INFLUENCE DE LA TEMPÉRATURE

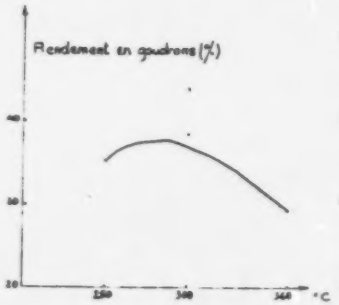
(Na_2CO_3 = 5,2 % ; 1/2 h ; pression initiale = 30 bars)

Taux de conversion (%)



°C

Rendement en goudrons (%)

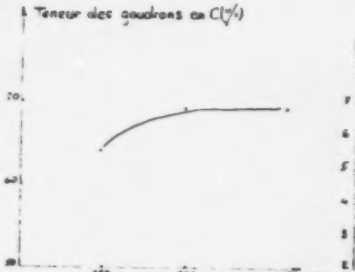


°C

Rendement énergétique (%)

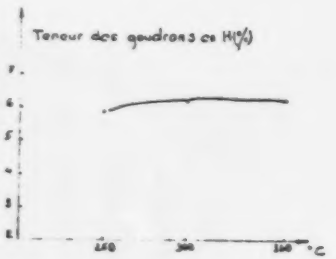
°C

Teneur des goudrons en C (%)



°C

Teneur des goudrons en H (%)



°C

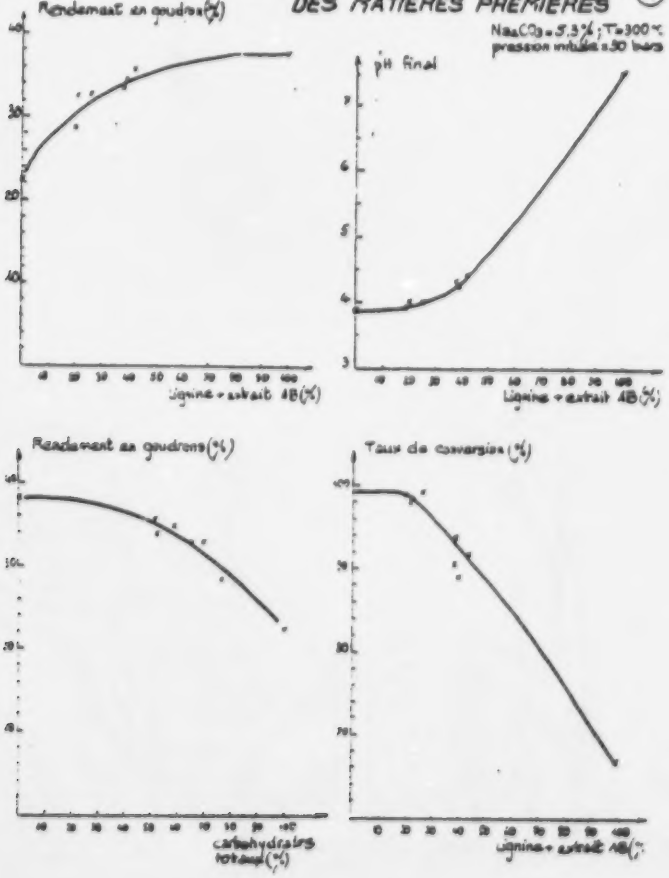
COMPOSITION CHIMIQUE DES MATIÈRES PREMIÈRES TRAITÉES EN HYDROLIQUÉFACTION

G

Nom	Nom scientifique	Provenance	Extrait alc.-benz. %	Extrait eau %	Lignine %	Carbohydrates (cell.+ pent.) %	Cendres %
Lignine sulfurique			0	0	96,5	0	1,5
Cellulose		coton	0	0	0	100	0
MECI	Fagraea schimus crassifolius	Nouvelle-Calédonie	3,6		15,3	76	1,15
BAGASSE		Guadeloupe	2,4	3,05	19,15	71,0	3,2
PEUPLIER	Populus sp.	France	2,9	2,15	22,25	66,3	0,4
ANGÉLIQUE	Dicorynia guianensis	Guyane	2,8	1,75	36,7	57,0	0,35
KOTIBÉ	Nesogordonia papaverifera	Côte d'Ivoire	4,0	2,8	34,1	52,15	1,9
DABEMA	Piptadenia africana	R.C.A.	9,8	1,7	27,8	55,4	0,5
WAPA	Eperua sp.	Guyane	17,5	3,2	25,7	50,8	0,8

INFLUENCE DE LA COMPOSITION CHIMIQUE DES MATIÈRES PREMIÈRES

H



A LOW PRESSURE-LOW TEMPERATURE PROCESS FOR THE CONVERSION OF WOOD TO LIQUID FUELS AND CHEMICALS

by

Shapour Afrashtehfar, Omar Ali, Norman Cooke,
David Cooper, Murray Douglas and Dixon Ng

Department of Chemical Engineering, McGill University
Montreal, Quebec, Canada, H3A 2A7

INTRODUCTION

The present contribution is based on the findings from two years of fundamental and exploratory research at McGill University on the liquefaction of cellulose (Sabade, S.B., 1983) and on our preliminary screening experiments with lignin and with wood (Douglas, W.J.M.). In particular, hydriodic acid has been shown to be remarkably effective in the depolymerization and deoxygenation of cellulose, bringing about appreciable formation of oil products and aqueous phase products. Bench scale batch studies were conducted at atmospheric pressure, on cellulose with aqueous HI solution, at temperatures up to 127°C, over a range of liquid-to-solid ratios and for reaction times from 30 to 24 hr.

Encouraging experimental results have been obtained when aqueous hydriodic acid is reacted with woodflour at 127°C and stochiometric ratio, R, of 5:1 (based on cellulose data) for reaction times from 1 min to 24 hr.

The objective of this project is to develop a feasible low-temperature, low-pressure process for the conversion of woods and similar cellulosic materials into

liquid hydrocarbons or near hydrocarbon products. A proposed process flow sheet is shown in Figure 1.

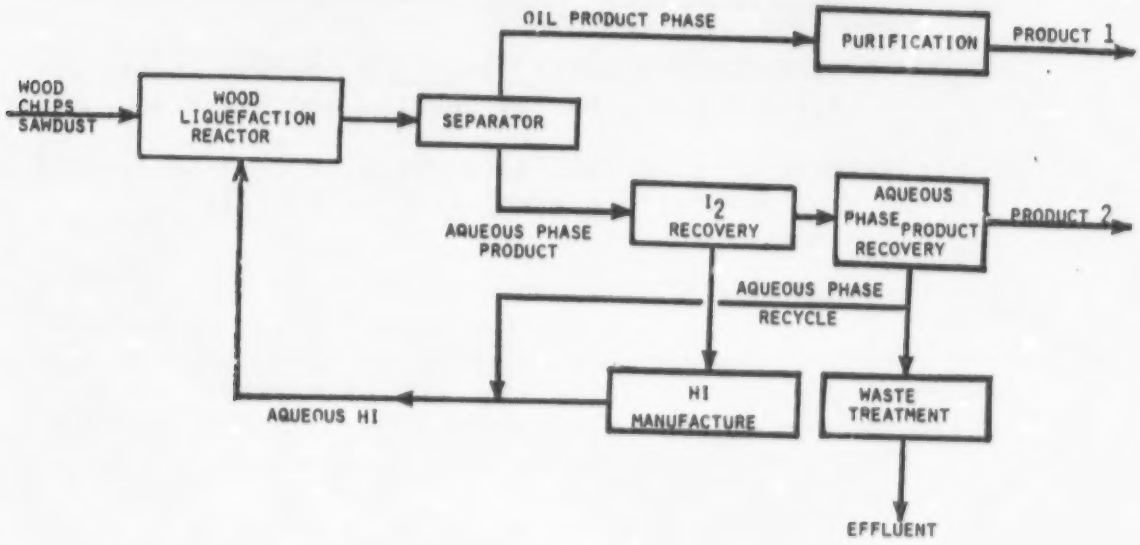


FIGURE 1. Proposed wood liquefaction Flowsheet of a continuous process

EXPERIMENTAL SECTION

1. Procedure

A schematic diagram of the experimental set-up is shown in Figure 2. One neck of the one litre three neck

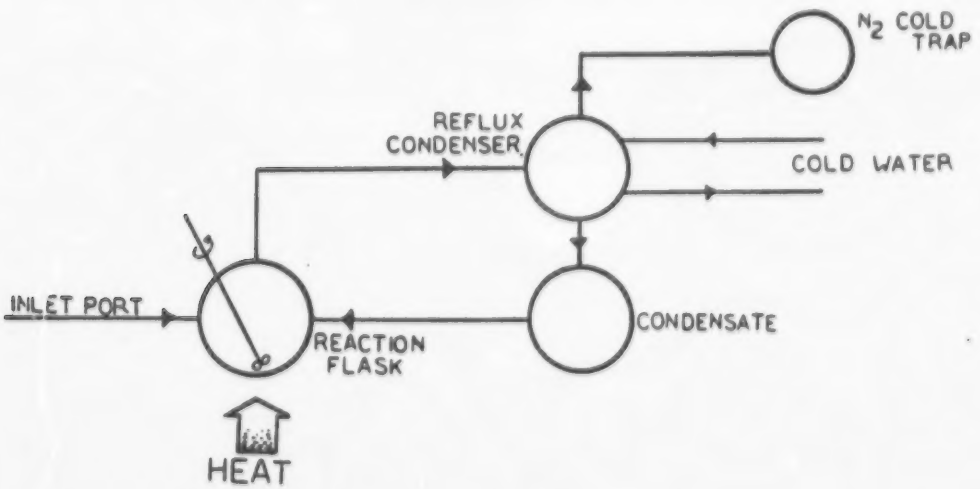


FIGURE 2. Schematic Diagram of Experimental Set-up

flask was enlarged to facilitate easy and fast introduction of the woodflour and cooling agent.

In a typical experimental run 143 ml (R = 5) of 58 Wt.% hydriodic acid (HI), suppied by Fisher Scientific, (containing approximately 1.5% hypophosphorus acid - H_3PO_2 - as preservative) was added to the flask along with three drops of H_3PO_2 and heated to its azeotropic boiling point - 127C. Five grams of black spruce woodflour (supplied by Pulp and Paper Research Institute of Canada, Pointe Claire, Que.) was quickly (<5s) introduced into the flask and allowed to react with the HI for a fixed reaction time. The woodflour was previously oven-dried at 80°C for two hours. A liquid nitrogen trap was installed, in a few runs, to investigate the extent of possible HI losses from the top of the condenser. Rapid quenching of the reaction was achieved by adding crushed dry ice to the flask.

The solid materials were separated from the aqueous phase by vacuum filtration (with chemical trap) and then transferred into a pre-weighed thimble. The aqueous phase was collected in two parts: the concentration portion, from the vacuum filtration step, was collected separately from the washings of the solid materials, Hirsch funnel and three-neck flask.

The thimble and contents were then freeze-dried and weighed. Ether and acetone extractions (with a SOXHLET extraction tube) were then sequentially carried out on the solid materials. In a few runs hexane, benzene, ether and acetone extractions were successively done. Known volumes of the aqueous phase were also freeze-dried in an effort to determine the solid content of the aqueous phase. The elemental analysis (C,H,I and O) of the products were done by Guelph Chemical Laboratories, Ontario.

2. Yield and Conversion Calculations.

Definition of the various yields used (weight % and iodine free basis) are presented below:

$$Y_{oil} = 100 \frac{\text{Weight of ether and acetone soluble product}}{\text{Weight of woodflour used}}$$

(yield of oil products)

$$Y_{res} \text{ (yield of residue)} = 100 \frac{\text{Weight of materials insoluble in ether \& acetone}}{\text{Weight of Woodflour used}}$$

$$Y_{oil(carbon)} \text{ (yield of carbon in oil products)} = 100 \frac{\text{Weight of carbon in oil products}}{\text{Weight of carbon in woodflour used}}$$

$$Y_{res(carbon)} \text{ (yield of carbon in residue)} = 100 \frac{\text{Weight of carbon in residue}}{\text{Weight of carbon in woodflour used}}$$

The extent of oxygen removal, EOR_{oil} (woodflour to oil product) was defined as:

$$EOR_{oil} = 100 \left(1 - \frac{\text{O/C ratio in oil product}}{\text{O/C ratio in woodflour used}}\right)$$

The conversion of the woodflour was defined as follows:

$$Y_{conv} = 100 \frac{\text{Weight of Woodflour - weight of residue}}{\text{Weight of woodflour}}$$

3. Analysis of the Aqueous Phase for its Iodine and Iodide Content(3)

The liberated iodine in the aqueous phase was determined with a standard solution of sodium thiosulfate.

$$I_2 + 2S_2O_3^{=} \rightleftharpoons S_4O_6^{=} + 2I^{-}$$

A 25 ml aliquot of the aqueous phase, in a 250 ml Erlenmeyer flask, was titrated with 0.1 N $Na_2S_2O_3$ to determine the iodine content. Triplicate runs were made. The endpoint was established by means of a starch solution indicator

The total iodine and iodide content of the aqueous phase was titrated, in the presence of a high concentration of hydrochloric acid, with a standard solution of potassium iodate. The iodine content found from the previous titrations was used to obtain the iodide content of the aqueous phase.

$$IO_3^- + 2I^- + 6Cl^- + 6H^+ \rightleftarrows 3ICl_2^- + 3H_2O$$
$$IO_3^- + 2I_2 + 10Cl^- + 10H^+ \rightleftarrows 5ICl_2^- + 5H_2O$$

A 5 ml aliquot of the aqueous phase was added to about 40ml concentrated HCl and 5 ml $CHCl_3$ in a 250-ml Erlenmeyer flask. The resulting mixture was titrated with 0.025F KIO_3 until the purple color from the chloroform disappeared. Triplicate runs were made.

RESULTS AND DISCUSSION

Several experimental runs, at fixed stochiometric ratio (R = 5) and HI concentrations (58 Wt %), were done for reaction times varying from 1 min to 24 hr.

1. Fractionation of the Products

The organic products are tentatively classified based on their solubility in aqueous HI, hexane, benzene, ether, and acetone (Criddle, W.J. and Ellis, G.P. 1967). Products soluble in aqueous HI are expected to be aliphatic carboxylic acids, polyhydric phenols, alcohols, and carbohydrates. When aliquots of the aqueous phases were freeze-dried, the resulting residues appeared generally dark red in color, in a syrupy state with a kind of sweet smell which is typical of carbohydrates and alcohols. Hexane- and benzene-soluble products are aliphatic and/or aromatic hydrocarbons which are perhaps iodinated. Ether- and acetone-soluble products vary from weakly to strongly polar compounds such as ethers, phenols, aldehydes, ketones, esters, and their iodinated derivatives. When the solvents were evaporated, these products appeared as a black fluid mixture. The residue of the reactions (which is insoluble in the above solvents) looked like a black conglomerate.

Modern analytical instrumentation such as GC-MS, HPLC, NMR and FT-IR will be employed towards the final characterization and identification of the reaction products extracted in the above-mentioned solvents.

2. Yield and Conversion.

For demonstration purposes, the results of a typical run (2 hr) are depicted in Figure 3. Shown in this figure are the elemental ratios (C,H,O and I) for the oil products, residue and aqueous phase products as well as the yields (iodine free basis) for the residue and oil products. The yields of solid products in the aqueous phase will be determined shortly, based on results from total organic carbon (T.O.C.) analysis. Comparison of the H/C and O/C ratio of the oil products to that of the woodflour revealed that the H/C ratio increased by approximately 45% while the O/C ratio dropped by approximately 60%. This decrease in the O/C ratio indicated that significant de-oxygenation had occurred. Comparisons of the H/C and O/C ratios of the residue to that of the woodflour showed increases of approximately 33% and 88% respectively.

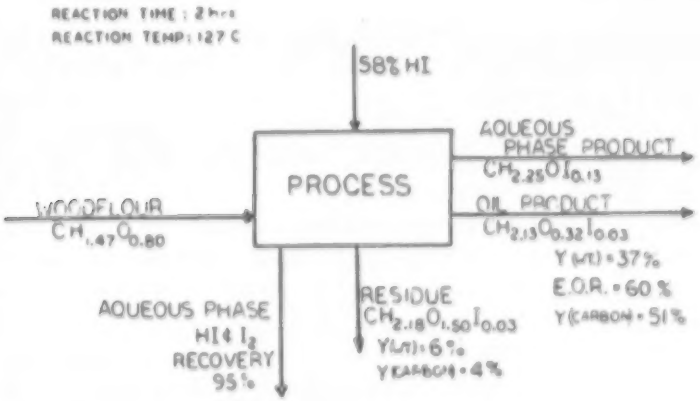


FIGURE 3. Fractions of a sample run

Carbon yields (iodine free basis) for the oil products and solid residue, at the different reaction times studied, are presented in Figure 4. The most promising reaction time seems to be in the 90 to 180 min range. These yields will be better when the carbon yields of the solid

products in the aqueous phase are included. It is interesting to note that the carbon yield of the oil product for the one minute reaction time is comparable to the yields obtained up to a reaction time of 90 minutes.

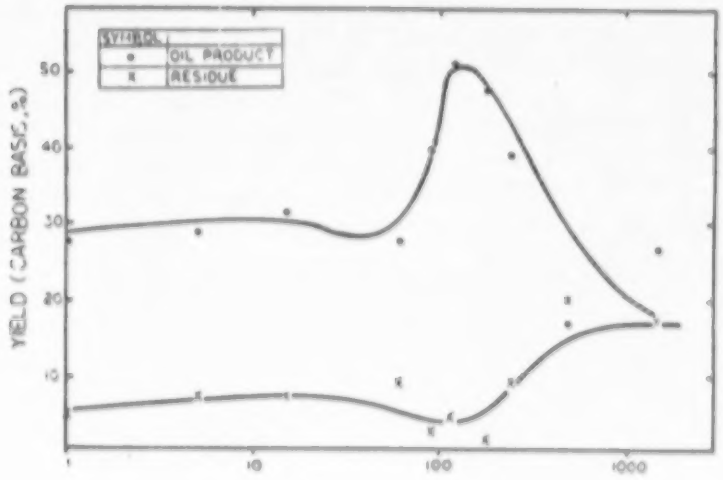


FIGURE 4. Reaction time (min)
Yield (carbon basis) of Oil Product & Residue

The conversion of woodflour (iodine free basis) is shown in Figure 5. Very high conversions are obtained throughout the time range with the peak being in the 90 to 180 minutes range. For longer reaction time (> 2 hrs) the conversion becomes smaller. This effect may be due to

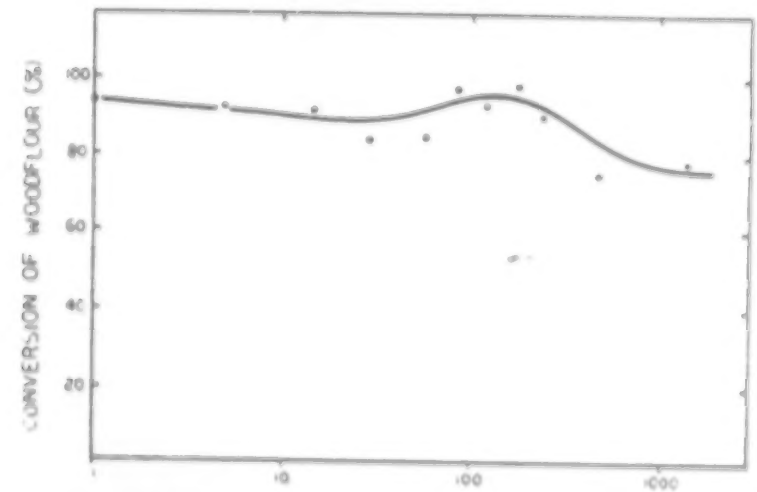


FIGURE 5. Reaction Time (min)
Conversion of Woodflour to Products

opposing reactions whereby the oil products are being converted to solid residue.

3. Compositions of the Products.

The elemental compositions of the oil products, solid residue and solid content of the aqueous phase are shown in Table 1. The elemental composition of the woodflour feed is $CH_{1.47}O_{0.80}$.

Table 1. Elemental compositions for solid products and extent of oxygen removal for oil products at different reaction times. Composition of woodflour is $CH_{1.47}O_{0.80}$.

Reaction Time (hr)	Elemental Composition			EOR % oil	Note
	Oil Products	Solid Residue	Aqueous Phase		
5/60	$CH_{1.85}O_{0.37}I_{0.01}$	$CH_{1.73}O_{1.02}I_{0.02}$	$CH_{2.13}O_{1.30}I_{0.18}$	54.2	a
15/60	$CH_{1.85}O_{0.54}I_{0.04}$	$CH_{1.32}O_{1.19}I_{0.02}$	$CH_{1.85}O_{0.56}I_{0.29}$	32.2	a
1/2	--	$CH_{1.79}O_{1.41}I_{0.02}$	$CH_{2.54}O_{1.32}I_{0.27}$	--	a
1	$CH_{2.2}O_{0.62}I_{0.006}$	$CH_{2.26}O_{1.57}I_{0.03}$	$CH_{2.28}O_{0.28}I_{0.31}$	22.4	a
2	$CH_{2.13}O_{0.32}I_{0.03}$	$CH_{2.18}O_{1.50}I_{0.03}$	$CH_{2.25}OI_{0.13}$	60.2	a
4	$CH_{2.11}O_{0.49}I_{0.06}$	$CH_{1.27}O_{0.86}I_{0.02}$	$CH_{2.81}O_{1.27}I_{0.16}$	38.3	a
8	$CH_{1.87}O_{0.73}I_{0.07}$	$CH_{1.32}O_{1.19}I_{0.02}$	$CH_{2}O_{0.50}I_{0.02}$	8.9	a
24	$CH_{1.85}O_{0.93}I_{0.08}$	$CH_{1.36}O_{1.27}I_{0.02}$	$CH_{2.65}O_{0.50}I_{0.24}$	46.8	a
1/60	$CH_{1.74}O_{0.63}I_{0.03}$	$CH_{1.35}O_{1.30}I_{0.01}$		20.7	b
1½	$CH_{1.52}O_{0.36}I_{0.02}$	$CH_{1.37}O_{0.90}I_{0.002}$		55.3	b
3	$CH_{1.66}O_{0.33}I_{0.03}$	$CH_{2.05}O_{0.94}I_{0.01}$		58.2	b

a Aqueous HI from a batch with 1.5% H_3PO_2.
b Aqueous HI from a batch with 2.6% H_3PO_2.

Comparison of the compositions of the oil products for all the runs (except the 24 hr run) with that of the woodflour shows a distinct lowering of the oxygen content and an increase in the hydrogen/carbon ratio. It should also be pointed out that the iodine content of the oil products are gratifyingly low for all the runs.

The oxygen content of the solid residues are much higher than that of the woodflour. This could be due to water contamination of the solid residue. As is the case of the oil products, the iodine content of the solid residue is also very low.

Also shown in Table 1 is the extent of oxygen removal (EOR_{oil}) for varying reaction times. Significant oxygen removal occurred during the 1½ to 3 hr range. The EOR_{oil} value at a reaction time of 5 min is also worth noting.

4. Iodine Balance

The iodine content (in the form of I_2, I^- and R-I, where R-I refers to the iodine content of the iodinated organic products) in all the phases, for each run, was accounted for. I_2 and I^- were only present in the aqueous phase and they were determined by titrations as described earlier. The amount of iodine combined with the organic products, in each fraction, was obtained from the Guelph microanalytical results in conjunction with the weight of the corresponding fractions.

Table 2 shows the results for iodine mass-balance for each run. The last column gives the amount of HI/I_2 lost during the laboratory procedures such as: refluxing HI with woodflour, and the subsequent vacuum filtration of the aqueous phase. It also carries 1% error due to volumetric measurements. Some modifications in the procedure has been made to minimize this loss and error in the future runs.

Table 2. Total iodine distribution (%) after different reaction times. R-I refers to the iodine in iodinated organic products.

Reaction Time (hr)	HI	I_2%	R-I%	Loss %	Note
5/60	86.3	8.69	0.75	4.26	a
15/60	82.0	10.4	1.34	6.26	a
1/2	85.2	7.81	-	-	a
1	81.0	6.35	1.44	11.2	a
4	84.3	9.69	0.90	6.11	a
8	80.5	7.52	0.78	10.3	a
24	81.5	9.50	1.01	8.00	a
1/60	98.8	1.32	1.09	-1.21	b
1½	95.1	0.56	0.33	4.01	b
3	94.7	0.56	0.33	4.41	

a Aqueous HI from a batch with 1.5% H_3PO_2 was reacted with the woodflour.

b Aqueous HI from a batch with 2.6% H_3PO_2 was reacted with the woodflour. It is interesting to note that the amount of iodine liberated in the latter case are markedly reduced.

5. HI Recovery

Preliminary laboratory tests have shown that 99% of the I_2 (in the aqueous phase) can be extracted very efficiently with 200 ml diethyl ether in three stages. The extracted iodine then may be reduced to HI by one of the following reactions and recycled into the HI stream.

$$H_2S + I_2 \rightleftharpoons S + 2H^+ + 2I^-$$
$$SO_2 + I_2 + 2H_2O \rightleftharpoons SO_4^{=} + 4H^+ + 2I^-$$
$$N_2H_4 + 2I_2 \rightleftharpoons N_2 + 4H^+ + 4I^-$$

It is interesting to note that about 83% of the HI, in most aqueous phases (Table 1), remains intact in the overall process. Based on this observation and the outcome of the current study on the role of I^- in the process, future work would be focussed on the OPTIMUM amount HI necessary.

PLANNED FUTURE WORK

1 To investigate the effect of process variables (temperature, liquid to solid ratio, concentration of reducing agent (I^-), H^+, etc), on the rate of liquefaction and the yield of oil products and aqueous phase by-products. At a fixed optimum reaction time - between 1 min and 3 hrs.

2. To perform further physical and chemical analyses to characterize the oil products and the aqueous phase products and to explore their potential uses.
3. To further investigate recovery and regeneration of the HI used in the process.
4. To recommend optimal operating conditions for conversion of wood to liquid products.

ACKNOWLEDGEMENTS

Financial support from the ENFOR Biomass Conversion Program of Energy Mines and Resources Canada is gratefully acknowledged.

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DIRECT CATALYTIC LIQUEFACTION OF BIOMASS

by

Lê H. Dao, Paul Hébert and André Houle

INRS-Energie
University of Quebec
C.P. 1020, Varennes, Québec
JOL 2PO

INTRODUCTION

The major objective of biomass liquefaction is the production of liquid fuels of high calorific value. Since the H/C ratio of biomass resources is generally in the same range as that of liquid hydrocarbon fuels, the key problem is to break down the cellulose and lignin polymers (depolymerisation) to fragments that can be converted to liquid by partial or total deoxygenation via reduction, hydrogenation, dehydration, decarboxylation, decarbonylation, rearrangement and other reactions.

Non catalytic pyrolytic liquefaction processes involve non selective radical reactions and give low quality liquids in poor yields. Better oil yields are obtained in direct liquefaction processes, however, even in this case, the oil has a poor quality since it tends to polymerize in storage and, being acidic, causes corrosion.

There are two approaches to the problems connected with poor oil quality. These are detailed study of the nature of the oil components causing instability and acidity and of the mechanism of their formation, and catalytic upgrading.

In our investigation of the nature and the origin of the oil components and their catalytic deoxygenation, we have concentrated on the chemistry of reactions accompanying the dissolution of biomass materials concomitant with the removal of oxygen.

EXPERIMENTAL

The raw material used in this study was spruce. The air dried wood was chipped and then ground with blender to pass a 0.35 mm screen. The flour was then dried over night in an oven at 110°C.

All experiments were carried out in a high pressure autoclave system (a schematic diagram is given in Figure 1). The autoclave was a conventional 1000 ml stainless steel autoclave (Autoclave Engineering, Ontario) with fixed head, removable lower unit and Magnedrive II stirrer; all external connections were through the head. Connections included a 1/8" stainless steel probe with shielded thermocouple for reading and controlling temperatures connected to a Omega controller (Model 300), a 1/4" sample injection and 1/8" product withdrawal water-cooled line, all below the liquid level. The stirrer dirve was a Cole Palmer Constant Speed and Torque Control Unit. The blade was a stainless steel catalyst basket with 9 stirring blades. A cooling coil was mounted inside the vessel in direct contact with the contents. A 50 gallons cooling water reservoir pressured to

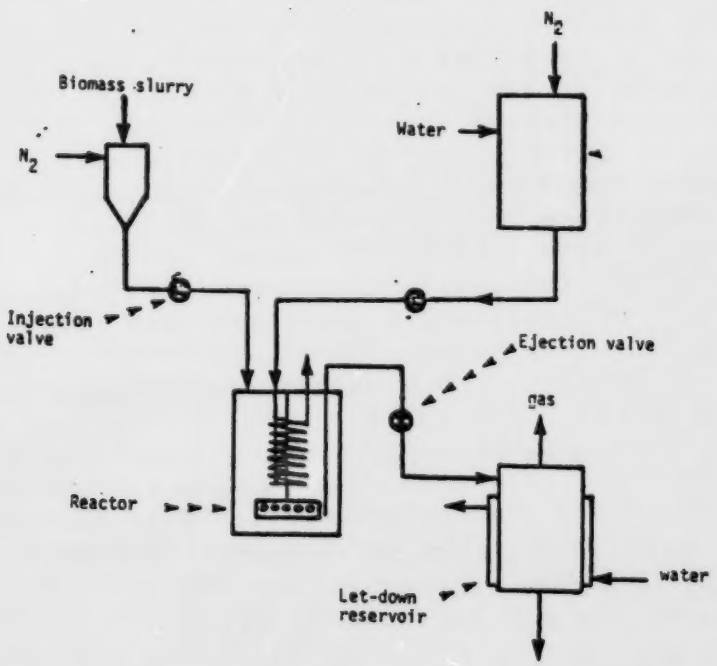

FIGURE 1. Short Residence Time Liquefaction Unit

150 psi with N_2 was also incorporated to give a high coolant flow rate. The injection system consisted of a heated stainless steel cylinder pressured up to 1000 psi with N_2 or other gas and a water-cooled ball injection valve. The reaction product was ejected from the autoclave by a water-cooled ball valve to a pressure let-down water-cooled stainless-steel reservoir. All lines throughout the system were fitted with appropriate vents, rupture discs, check valves, pressure gauges, etc. The following procedure was followed for the reactions. The unit was flushed with N_2. Heating with an electric heater was then initiated. As the desired operating temperature was reached, the injection system was sequentially loaded with a slurry of 25.00 g dried wood and 250 ml of a solution containing the desired quantities of catalyst and water, and 50 ml of water heated to 80°C. The stirrer was started (500 rpm) and then the injection valve was opened.

The injector was pressured to ~ 300 psi, and the contents forced into the vessel in about 2-4 sec. The temperature drop under these conditions was generally 100-150°C. Recovery to the desired temperature required about 0.6-1 minute; reaction time was assumed to start when the injection valve was opened. The pressure rose rapidly and stabilized after less than 1 minute. At the end of the run after the required reaction time, the heater was shut down and the contents ejected from the heating zone in 10 sec to a let-down water-cooled reservoir. Generally, the temperature of the product mixture dropped rapidly from 350°C to 150°C in less than 30 seconds, and to 90°C in 1 minute. The gas vented into a water-filled graduate cylinder and measured. Samples were taken for IR, GC and MS. The autoclave was washed twice with 300 ml of water at 300°C. The liquid products which consisted of an aqueous phase (the pH was checked and neutralised if necessary) and an oil phase were extracted in a continuous liquid extractor over night with 200 ml of CH_2Cl_2. The system was cooled down and the autoclave opened. The walls of the reactor and the let down reservoir were washed with acetone and filtered. The two organic factions were evaporated and the total combined mass used to calculate the percentage yield of oil, based on the mass of wood used. The acetone insoluble fraction was assumed to be char.

A typical time temperature profile of a wood slurry in water is shown in Figure 2.

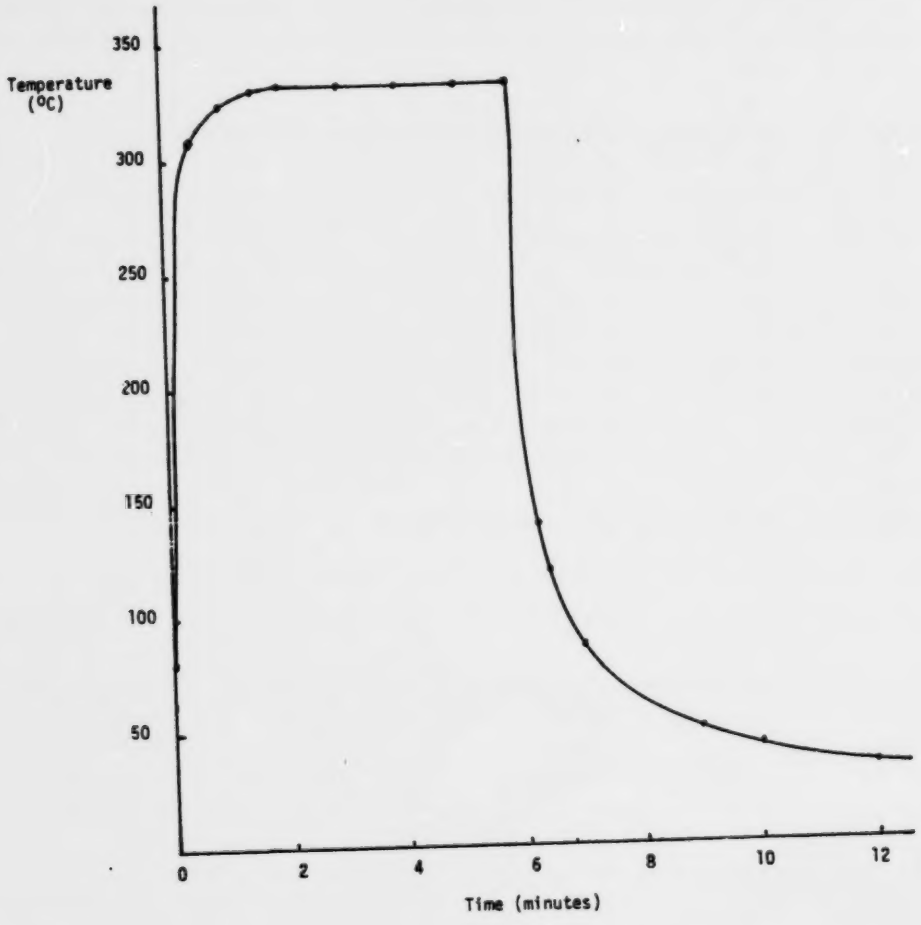

FIGURE 2. Typical Time-temperature profile

RESULTS AND CONCLUSIONS

the results are contained in Tables, 1, 2, 3, 4. The major conclusions are:

- With sodium formate as catalyst (Table 2), the higher temperature decreases the oil yield but reduces the oxygen content of the oil (increase of heat of combustion). Prolonging the reaction (Table 1) decreases the oil yield but doesn't raise much the heat of combustion by very much.

- Silica-alumina catalyst appears to have no effect on the yield of the liquefaction (Table 3).

ACKNOWLEDGEMENT

The authors gratefully acknowledge financial support from Imperial Oil Limited (University Grants), NSERC, FCAC and INRS.

Table 1. Influence of residence Time at 335°C

Catalyst	Gas	Time (min)	Oil yield %	Tar yield %	ΔHc MJ/kg
HCO_2Na	N_2	5	27	4	29.54
HCO_2Na	N_2	15	25	9	30.35
HCO_2Na	N_2	30	24	9	31.19

Table 2. Influence of temperature at 5 minutes of residence time

Catalyst	Gas	Temperature °C	Oil yields %	ΔHc MJ/kg
HCO_2Na	N_2	313	27	29.54
HCO_2Na	N_2	335	27	29.54
HCO_2Na	N_2	348	20	32.56

Table 3. Influence of alumina-silica catalyst

Catalyst	Gas	Temperature °C	Time	Oil yields	ΔHc MJ/kg
$CO_2Na/AL_2O_3-SiO_2$	N_2	318	5	23.4	29.30
$CO2Na/AL_2O_3-SiO2$	N_2	324	5	24.2	29.54

Table 4. Influence of acid-catalyst

Catalyst	Gas	Tempereture °C	Time (min)	Oil yield %	Tar yield %	ΔHc MJ/kg
HCl	N_2	306	5	41.0	9	26.56
HCl-Fe	N_2	315	5	40.0	9	26.01
$FeCl_3$	N_2	300	5	16.0	18	26.98
SK500	N_2	314	2	40.2	11	28.70
SK500	N_2	315	5	38.6	12	30.03
SK500	N_2	315	9	35.6	13	30.65
SK500	N_2	315	15	32.0	12	31.01
SK500	N_2	315	20	31.5	12	31.93
MH	N_2	313	2	39.9	7	29.08
MH	N_2	313	5	37.4	7	29.20
MH	N_2	313	10	31.8	9	29.57
MH	N_2	313	15	28.0	10	30.87
MH	N_2	313	20	28.2	11	31.34
HCO_2H/MH	N_2	340	5	38.0	--	30.39
HCO_2H/MH	N_2	350	5	40.0	--	30.39

Section 3

SUPERCRITICAL FLUID EXTRACTION

LIQUEFACTION OF POPLAR WOOD AND PEAT BY SUPERCRITICAL FLUID EXTRACTION

Elizabeth C. McDonald, Bridie Bennett
and John Howard
B.C. Research
3650 Wesbrook Mall
Vancouver, B.C.
V6S 2L2

INTRODUCTION

At the ENFOR Specialists Meeting on Biomass Liquefaction held in February, 1982, the results of supercritical fluid extractions of western red cedar were reported. Oil yields of 70% based on dry feed were obtained at a temperature of 360°C and a pressure of 28 MPa with both supercritical acetone and methanol. At 10 MPa and 360°C, oil yields were 50% with acetone and 40% with methanol. Similar results were obtained with hemlock. Extractions of red alder hardwood gave products which were less viscous than softwood-derived oils and, at extraction conditions of 260°C and 10 MPa, the yield was about a third of that obtained from softwoods (McDonald, 1981,1982).

Analysis of the extract and residue from western red cedar using supercritical methanol showed that methanol had reacted with the wood. No evidence was found of a similar reaction of the wood with supercritical acetone and condensation products of acetone were not found in the oil. An economic analysis showed that the cost of producing wood oil was sensitive to loss of solvent in the process and, consequently, acetone was indicated as the preferred supercritical fluid.

To permit the comparison of oils produced from a variety of processes using different feedstocks, the International Energy Agency proposed a comparative test program of liquefaction processes using standardized feedstocks of poplar wood and peat. B.C. Research was invited to submit oils produced by supercritical fluid extraction for inclusion in this program.

EQUIPMENT

Modifications were made to our existing equipment to measure the reaction temperature and heating rate, and to prevent loss of acetone at the start of the run. The equipment is shown schematically in Figure 1.

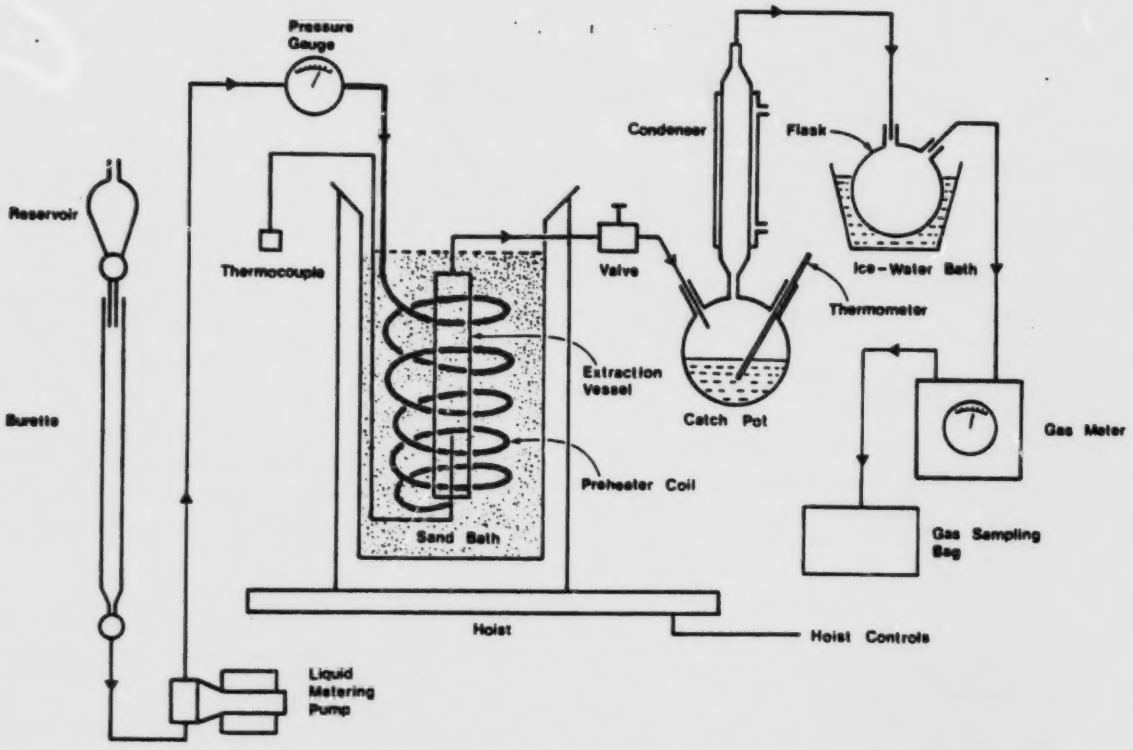

FIGURE 1. Supercritical Acetone Extraction of Poplar Wood and Peat: Schematic of Equipment

A thermocouple was inserted through the base of the double-ended autoclave to about one-third of the height of the autoclave. The sand bath was maintained at 350 ± 5°C during the extraction and was preheated to 370°C before immersion of the autoclave. About 12 minutes were required for the contents of the autoclave to reach the reaction

temperature of 350°C, as shown in Figure 2. We had anticipated a faster heating rate because the acetone was preheated in a coil in the sand bath and was pumped continuously from the time of immersion of the autoclave.

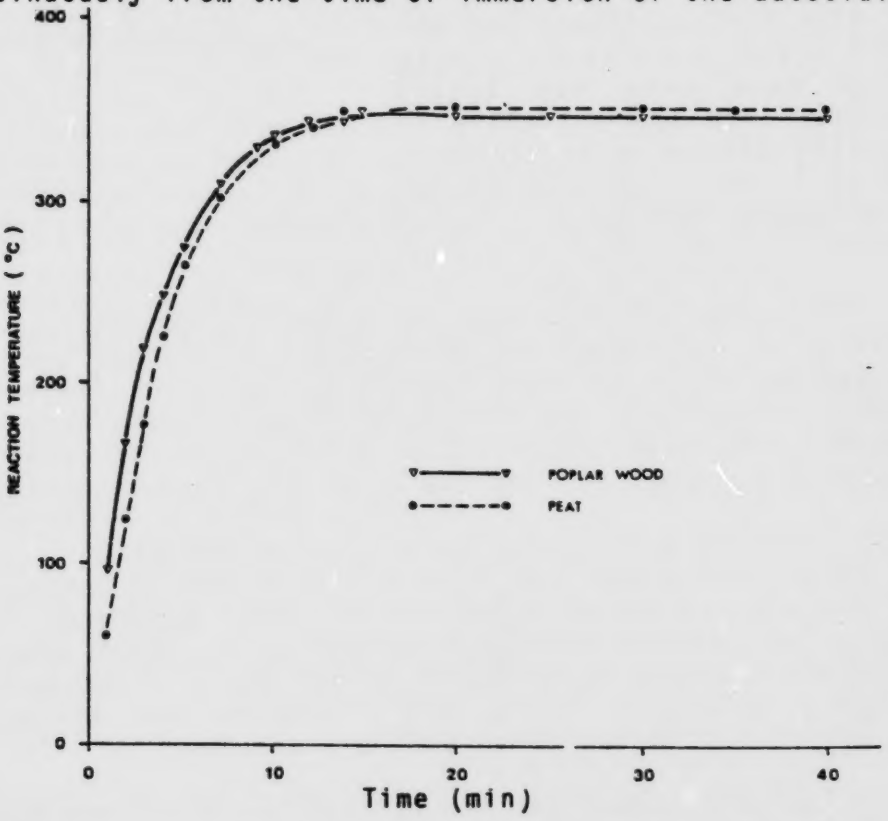

FIGURE 2. Reaction Temperature during the Supercritical Extraction of Poplar Wood and Peat

A hoist was built to raise the sand bath so that the autoclave and catch pot could be securely connected prior to immersion of the autoclave. Previously, the autoclave was lowered into the sandbath and solvent was lost while connecting the catch pot.

EXTRACTIONS OF POPLAR WOOD

The BLTF, IEA Standard wood described by Beckman on page 4 of these proceedings.

To accomodate the dimensions of our autoclave (0.1 L) chips were cut into pieces of about 15 x 3 mm. Fifteen to twenty grams of wet wood, with a moisture content of 10.4 percent, were packed into the autoclave for each extraction. The autoclave was sealed, connected to the solvent line and catch pot, and about 50 ml of acetone pumped into the cold autoclave. with the valve closed, the preheated sand bath was raised. Acetone was pumped continuously into the autoclave and the pressure controlled by adjusting the valve on the exit arm. The extraction was stopped after 30 to 40 minutes when the extract was clear. The temperature inside the reactor was measured throughout the run.

Oil and acetone were collected in the air-cooled catch pot at a temperature of 35 to 40°C. Less than 1 ml of acetone was collected in the ice-water cooled flask after the condenser. The solvent was evaporated in a rotary evaporator at 25°C and the weight of wet oil determined. Gas samples were analyzed for CO_2, CO, CH_4 and H_2 by gas chromatography.

Eighteen extractions were carried out at 350°C and 10 MPa, to produce about 140 g of oil (dry basis). Most of the oil was sent to Battelle Pacific Northwest Laboratory for analysis. Four extractions were carried out at 350°C and 28 MPa to produce about 70 g of oil. Analyses for elemental composition, calorific value, water content and ash were carried out at B.C. Research on each oil sample.

Table I summarises the extraction conditions and analysis of products. The conversion of poplar wood to liquid and gaseous products and the yield of oil at each pressure are similar to the western red cedar extraction results. At 10 MPa, the yield of poplar wood oil was 43% and at 28 MPa, the yield was 73%. At 10 MPa, the recovery was calculated at 77% and there is no apparent explanation for this low result. Inclusion of the water produced in the process by pyrolysis reactions would increase the recovery at 10 MPa to 90 Percent and the recovery at 28 MPa to 110 percent. The water produced was calculated by substracting the water content of the feed from the water content of the acetone/oil extract (determined by Karl Fischer titration).

Table I. Supercritical Acetone Extraction of Poplar Wood: Summary of extraction conditions and product analysis

PARAMETER	Unit	Batch 1	Batch 2
Reaction Pressure	MPa	10	28
Reaction Temperature	°C	350	350
Reaction Time	Minute	27	35
Kg feed/run	kg maf[1]	0.015	0.016
Moisture content of feed	%	10.4	10.4
Ratio acetone/feed	kg/kg maf	14.8	13.8
Heating rate	°C/min	25	27
Yield[2], kg oil maf/kg feed maf	%	43	73
Conversion, (kg feed-kg residue)/kg feed	%	72	92
Recovery, (kg oil (maf) + kg gas + kg residue)/ kg feed (maf)	%	77	90
Water produced by pyrolysis, kg/kg feed	%	9.1	22.3
Analysis of Extract			
Carbon	% maf	63.2	71.4
Hydrogen	% maf	7.54	7.63
Nitrogen	% maf	0.19	0.17
Oxygen	% maf	28.7	18.5
Ash	% maf	0.28	0.06
Water in raw product	%	13.3	3.23
Calorific value	MJ/kg maf	27.3	31.2
Analysis of Gas Produced			
Carbon dioxide, kg/kg feed	%	5.2	6.2
Carbon monoxide, kg/kg feed	%	1.5	1.5
Hydrogen, kg/kg feed	%	0.01	0.02
Methane, kg/kg feed	%	0.04	0.17
Analysis of Residue			
Carbon	%	77.9	70.7
Hydrogen	%	4.99	4.84
Nitrogen	%	0.23	0.24
Oxygen	%	16.88	24.22

1. maf = moisture and ash free.
2. Corrected for the weight of acetone condensation products (Table II).

Charring of the residue occurred at 10 MPa, but not at 28 MPa for the poplar wood extractions, which is in contrast to the cedar extractions which did not produce charring at either pressure.

The amount of extract recovered was greater than that reported as percent oil yield in Table I because of acetone condensation products formed during the extraction. The raw products were analyzed by gas chromatography for diacetone alcohol and mesityl oxide and, as shown in Table II the extract at 10 MPa was found to contain 12.9 percent by weight of these compounds. At 28 MPa, the extract contained 34 percent of these compounds. The oil yield was calculated after subtracting the weight of water, ash and acetone byproducts from the weight of raw product. the carbon and oxygen contents of the oils, shown in Table 2, reflects the greater amount of mesityl oxide in Batch 2 over Batch 1 since this compound has a carbon content of 73.4 percent and oxygen content of 16.3 percent. as shown in Table II, the cedar extract did not contain significant amounts of acetone condensation products.

Table II. Supercritical Acetone Extraction of Poplar Wood: Analysis of oil for Acetone and Acetone Condensation Products

Compound	Batch 1 10 MPa, 350°C, wt.%[1]	Batch 2 28 MPa, 350°C, wt.%	Western Red Cedar 10 MPa, 350°C wt. %
Diacetone Alcohol	2.2	0.94	0.69
Mesityl Oxide	10	33	0.79
Acetone	0.7	0.28	N/A[2]
Total Weight of Acetone and By-Products as a Percentage of Extract	12.9	34	1.48
Acetone Consumed as a Percentage of maf Oil[3]	20	70	1.5

1. Extract after evaporation of acetone in rotary evaporator: contains water, ash and wood oil.
2. Data not available.
3. (kg acetone consumed/kg maf oil) x 100: diacetone alcohol and mesityl oxide concentrations converted to equivalent weight of acetone consumed.
   kg maf oil = kg total extract - (kg water + kg ash + kg acetone, diacetone alcohol and mesityl oxide)

The presence of acetone condensation products in the poplar wood oils may be due to the formation of acetic acid during the pyrolysis reactions which acid catalyzed the condensation reactions to form diacetone alcohol and mesityl oxide. While plicatic acid is present in cedar at room temperature, it is known to form a lactone (plicatin) at nigh temperatures and would not be available to act as an acid catalyst during the supercritical acetone extraction. It is, therefore, thought that the formation of acetone condensation products is dependent on the wood species. the formation of large amounts of acetone condensation products was not anticipated from the results of our previous work. It is now apparent that methanol would have been a more suitable supercritical fluid for liquefaction of poplar wood.

The amount of acetone consumed in the process by reaction to form diacetone alcohol and mesityl oxide, as a percentage of wood oil produced, was 20% at 10 MPa and 70% at 28 Mpa (Table II). Based on our previous economic analysis of the process, the cost of producing poplar wood oil by supercritical fluid extraction using acetone would be uneconomic as a result of these solvent losses.

EXTRACTIONS OF PEAT

The standard IEA BLTF peat feedstock originated in Finland. The analytical is given by Beckman on page 5.

The same equipment and procedure were used for the peat extractions as for the poplar wood extractions. The peat, with a moisture content of 49.6 percent, was used as received. approximately 50 g of wet peat was packed into the autoclave for each extraction. Three extractions were carried out at 350°C and 10 MPa to produce about 40 g of waxy extract. A heterogeneous extract was obtained consisting of a liquid and a waxy solid.

Two extractions were carried out at 350°C and 28 Mpa. The first of these extractions was carried out on the peat as received and the extract looked identical to that obtained at the lower pressure. The second extraction at 28

MPa was performed with diatomaceous earth (15 g) intimately mixed with the wet peat (30 g). The extract from this run was markedly different to the other peat extracts, being a homogeneous, low viscosity oil. Budget constraints prevented further experiments to investigate the effect of diatomaceous earth on the peat oil produced.

The experimental conditions and product analysis for the extractions at 10 MPa and the extraction at 28 MPa in which diatomaceous earth was mixed with the peat are presented in Table III.

In the heterogeneous extract produced at 10 MPa, acetone condensation products were present mainly in the waxy solid and 7.8 percent by weight of mesityl oxide was found in this material. The elemental analysis of the solid reported in Table III includes the contribution of the mesityl oxide. Small amounts of diacetone alcohol and mesityl oxide were also present in the aqueous phase. The acetone consumed was calculated to be 0.1 kg for each kg of oil produced (10 percent w/w). The results of this work show that a supercritical fluid, such as methanol, which does not form condensation products should be used for the liquefaction of peat.

The peat oil yield was calculated from the weight of the solid phase after subtracting the weight of mesityl oxide. The yield is greater than the conversion, which indicates that either the yield has been overestimated or the conversion underestimated. This may be caused by a number of factors. First, the water content of the oil was not measured because, based on the appearance of the oil, the water content was assumed to be negligible. Second, acetone may have reacted with either the oil or the residue to form polymers of greater molecular weight than the dimers analyzed.

The oil produced when Celite^{TM} was mixed with peat had markedly different characteristics, not only in appearance but in elemental composition (Table III). the overall moisture content of this oil was the same as that for the raw product without the addition of Celite, yet a one phase product was obtained. The amounts of diacetone alcohol and mesityl oxide present in the oil were not measured. the different characteristics of this oil could result from the catalytic action of metals, such as iron, on the surface of the Celite.

Table III. Supercritical Acetone Extraction of Peat: Summary of Extraction Conditions and Product Analysis

Parameter	Unit	Batch 3 wet peat as received		Batch 4 Celite™ (15g) mixed with wet peat
Reaction Pressure	MPa	10		28
Reaction Temperature	°C	350		350
Reaction Time	Minute	23		30
Kg feed/run	kg maf[1]	0.024		0.014
Moisture Content of feed	%	49.6		49.6
Ratio Acetone/Feed	kg/kg maf	8.6		15.7
Heating Rate	°C/min	24		21
Yield, kg oil maf/kg feed maf	%	55[2]		51[3]
Conversion, (kg feed - kg residue)/kg feed	%	45		75
Recovery,[4] (kg oil (maf) + kg residue)/kg feed maf	%	110		76
Acetone consumed, kg/kg maf oil	%	10		N/A
Analysis of Extract		Solid	Liquid	
Weight of solid and liquid as percent of raw product	%	53	47	(one-Phase)
Water in raw product	%	N/A[5]	82	39
Diacetone alcohol content	wt. %	nil	0.46	N/A
Mesityl oxide content	wt. %	7.8	0.43	N/A
Carbon	% maf	66.93	8.31	75.1
Hydrogen	% maf	9.60	10.67	8.35
Oxygen[6]	% maf	20.93	80.13	13.7
Nitrogen	% maf	2.54	0.89	2.81
Ash	% maf	0.37	N/A	N/A

1. maf = moisture and ash free.
2. Semi-solid poroduct only, corrected for acetone condensation products.
3. Moisture free extract, not corrected for acetone condensation products.
4. Excluding gas which was not analyzed.
5. Not analyzed.
6. Calculated by difference.

CONCLUSION

Supercritical acetone extractions of standardized poplar wood and peat feedstocks were carried out at 350°C and pressures of 10 and 28 MPa. The yield of poplar wood oil was 43 percent at 10 MPa and 73 percent at 28 MPa, comparable yields to those obtained in previous work with supercritical acetone extractions of western red cedar. However, in contrast to the cedar extractions, acetone reacted to form condensation products during the poplar wood extractions and diacetone alcohol and mesityl oxide were identified in the extracts.

Extractions of peat resulted in a heterogeneous product composed of an aqueous phase and waxy solid. Acetone reacted during the peat extractions to form predominantly mesityl oxide which was associated with the waxy solid. The extraction of a mixture of peat and diatomaceous earth gave a markedly different homogeneous product.

The formation of condensation products shows that supercritical acetone is not a suitable fluid for the liquefaction of either poplar wood or peat. A supercritical fluid, such as methanol, which does not undergo these reactions should be used in future liquefaction work.

ACKNOWLEDGEMENT

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PRODUCTION OF PYROLYTIC OILS FROM ASPEN WOOD BY DENSE GAS EXTRACTION

S. KALIAGUINE, H. DANIEL AND J.L. GRANDMAISON
DEPARTMENT OF CHEMICAL ENGINEERING
UNIVERSITÉ LAVAL, QUÉBEC, QC, CANADA
G1K 7P4

INTRODUCTION

In our laboratory we have undertaken a series of studies of the liquefaction of wood by Dense Gas Extraction. These studies are not aiming at a search of optimal conditions for an eventual large scale process working on this principle. Our goal is to get some insight into the intricacy of the physico-chemical phenomena involved in the pyrolysis of wood. Dense Gas Extraction is of some interest in this context because it (hopefully) does not involve additional chemical reactions of the products with either gaseous reactants or catalysts. It also allows the variation of the conditions of the mass transfer phenomena by varying the nature of the solvent and its pressure, and thus allows the study of the coupling of mass transfer with pyrolysis of the solid structure. Moreover it simplifies the heat transfer process to the reacting matrix of the wood by imposing conduction from the solvent as the only heat exchange to and from the wood.

As a first study conducted in methanol is already available in the literature (Labrecque et al 1984, Labrecque, 1983), I will just recall some of the results and conclusions and compare them with more recent data obtained with n-pentane, benzene and tetrahydrofuran as solvents.

Figure 1 is a schematic sketch of our set-up. About 40 g of wood under the form of neatly cut cubes of known dimensions, is placed in a spinning basket inside a 750 ml autoclave. The high pressure solvent is continuously fed to this autoclave, the temperature of which can be programmed as a funtion of time. Oil is therefore continuously withdrawn from the autoclave as a solution which passes through an expansion valve and a condenser. Successive fractions of the oil can thus be collected as the temperature of the autoclave is raised. The solvent in each fraction is then evaporated at 75°C under vacuum and the mass of oil is recorded. This evaporating procedure provides an oil essentially free from solvent (the peak of methanol can be essentially eliminated from a proton NMR spectrum of the oil) and from water (0.3 to 0.5% of water is usually measured).

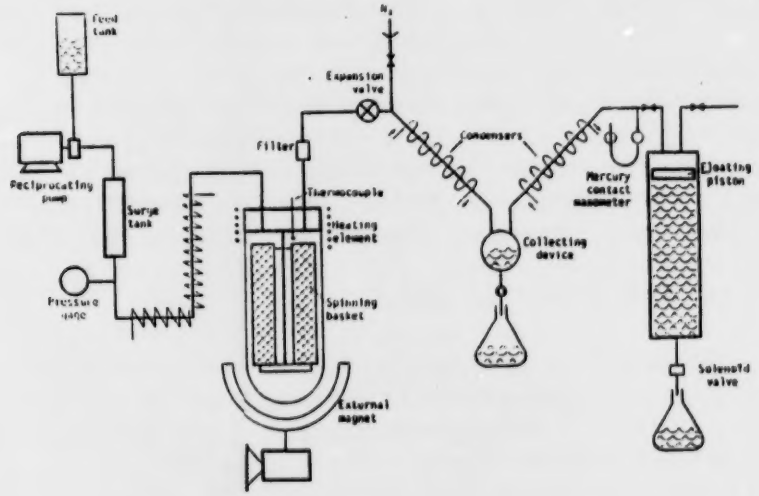

FIGURE 1. Schematic Diagram of the Experimental Set-up

The cumulative mass of oil is shown on figure 2 as a function of the time of extraction. In a typical experiment we produce two fractions designated as oil N° 1 and oil N° 2 collected respectively before and after the end of the first plateau. The oxygen content is in the range 27-33 mass % for oil N° 1 and between 32-37 % for oil N° 2. The four curves

on figure 2 correspond to four experiments performed under comparable conditions in each of the four mentioned solvents.

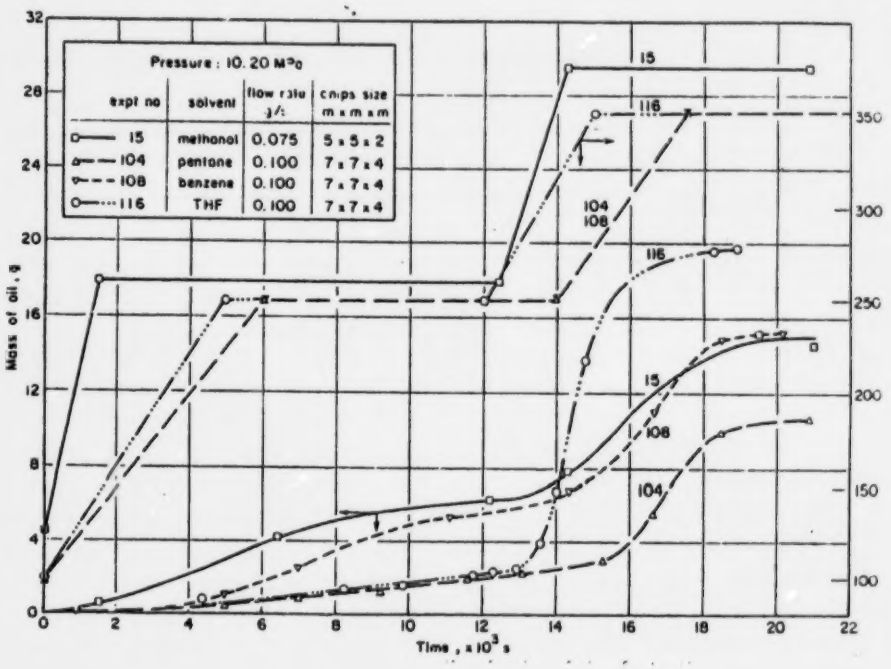

FIGURE 2. Mass of Extracted Oil as Functions of Time of Extraction

The temperature program which we systematically adopted in these experiments involves two plateaus at about 250 and 350°C. This program is intended to permit collection first of the pyrolysis products of hemi cellulose and lignin, and secondly of those of cellulose.

It can be seen from this figure that the four solvents have different behaviour in the two extractions. For the low temperature extraction the yields are in the order methanol > benzene > THF > n-pentane, whereas for the high temperature extraction the order is: THF > methanol > benzene > n-pentane.

It seems thus, that for the second extraction the solvents efficiency is in the order of their normal solubilities, (THF being know as a better solvent than methanol), whereas for the first extraction this is not the case. To explain this different behaviour we refer to the data of Morgan and Orsler (1969) on the swelling behaviour

of beech and podo woods in organic solvents. The authors measured the final equilibrium percentage swelling in the longitudinal (L), radial (R) and tangential (T) directions with respect to the dry dimensions and the $t_{\frac{1}{2}}$ taken to reach half the final T value.

Table I. Swelling behaviour in various solvents (Morgan & Osler 1969)

	Beech				Podo			
Solvent	L	R	T	$t_{\frac{1}{2}}$	L	R	T	$t_{\frac{1}{2}}$
water	0.9	6.6	16.7	instant	2.7	2.5	6.8	instant
methanol	0.9	6.4	15.0	"	2.4	2.1	6.2	"
THF	0.5	5.0	11.1	6 hr	1.3	2.0	5.5	40 hr

As can be seen from table I, these data indicate that methanol is a better and a faster swelling agent than THF. In agreement with the conclusions of Hansen and April (1982) we would therefore relate the efficiency of the low temperature extraction of hemicellulose and lignin, to the ability of the solvent to swell the wood, that is to reach these components by loosening the texture of the cellulose fibers. To be efficient in this first extraction, a solvent is therefore thought to be able to break the hydrogen bonds linking the cellulose fibers together.

Figure 3 presents some data obtained with methanol at various pressures and a nominal flow rate of 0.16 g/s. The three dependent variables are defined as follows:

- wood conversion $X = 1 - \frac{\text{mass of char at 350°C}}{\text{initial mass of dry wood}}$

- total oil yield $R_T = \frac{\text{mass of evaporated oil at 350°C}}{\text{initial mass of dry wood}}$

- oil yield at 250°C $R_1 = \frac{\text{mass of oil collected at 250°C}}{\text{initial mass of dry wood}}$

The curves for X and R_T are in agreement with

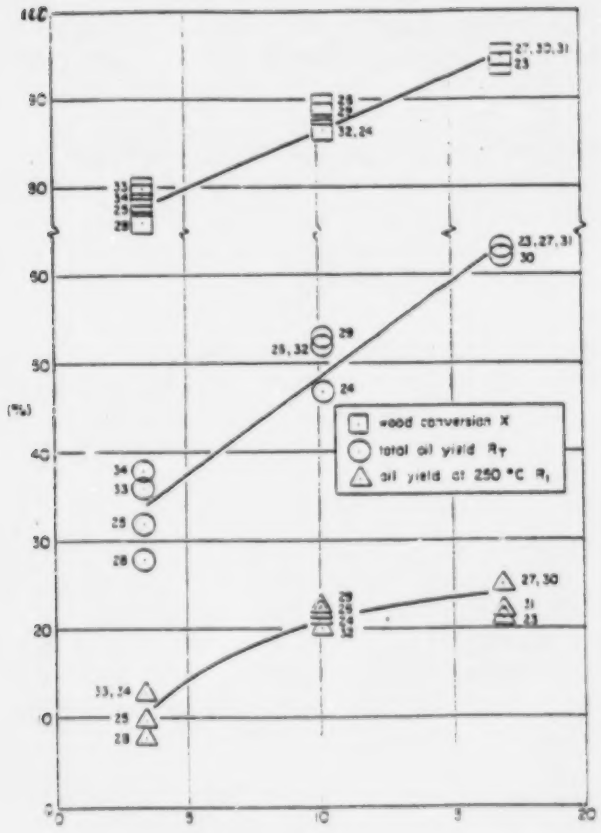

FIGURE 3. Wood conversion and Oil Yields as Functions of Pressure Solvent: Methanol

similar results obtained in methanol by McDonald and Howard (1981). A steep increase of both R_T and X with pressure corresponds to a continuous increase in solubility for the oil components as pressure is increased in the dense gas region (Randal 1982) (Procaccia and Gitterman, 1983). Interestingly the difference (X - R_T) which can be considered as a rough estimate of the yield in volatile compounds formed at 350°C, is decreasing as pressure is increased (from 43 to 32% between 3.40 and 17.0 MPa). This suggests that improving

its extraction protects a given compound from secondary pyrolysis reactions, or otherwise expressed, that pyrolytic fragmentation of this compound is faster in the char than in the solvent. There could be two explanations for such a behaviour: the char could be at a higher temperature than the solvent or the fragmentation could be a bimolecular reaction.

We favor the second explanation because we have shown (Labrecque et al 1984) that a eight-fold increase in the RPM of the basket has no significant effect on X or R_T which suggests the absence of a significant thermal gradient at the char-solvent interface.

As is also shown on figure 3, R_1 increases with pressure which confirms that with methanol the first extraction is also governed by the thermodynamic equilibria of solubility.

Similar results obtained with THF are presented on Figure 4. The Variations for X and R_T are similar to those observed with methanol. R_1 however behaves differently in THF: it is almost constant and even slightly decreasing with pressure. The fact that this extraction is not affected by the increase in solubility of the solvent with pressure is another indication that the poor wood swelling properties of THF prevent solubilization.

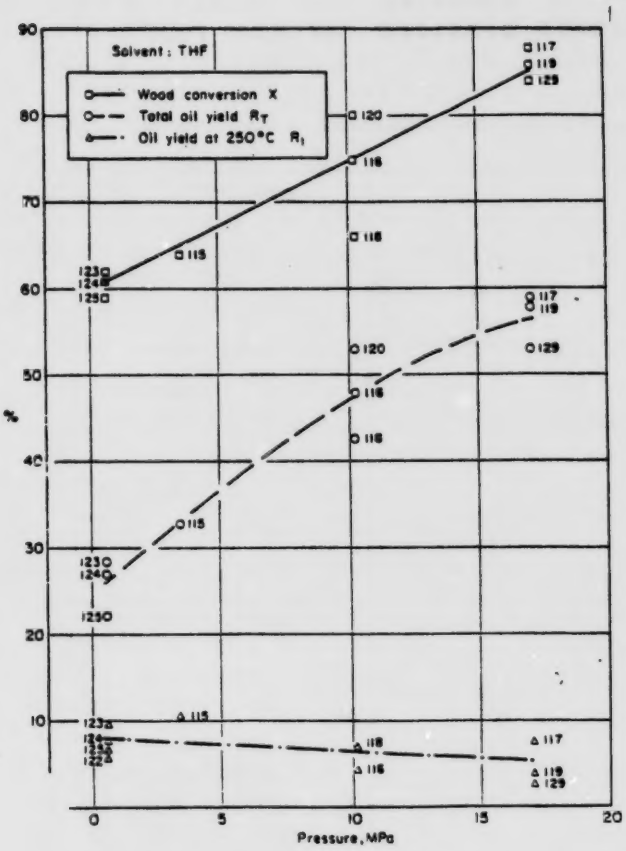

FIGURE 4. Wood Conversion and Oil Yields as Functions of Pressure Solvent: THF

Figure 5 compares the influence of solvent flow rate at a constant pressure for the four solvents. In all

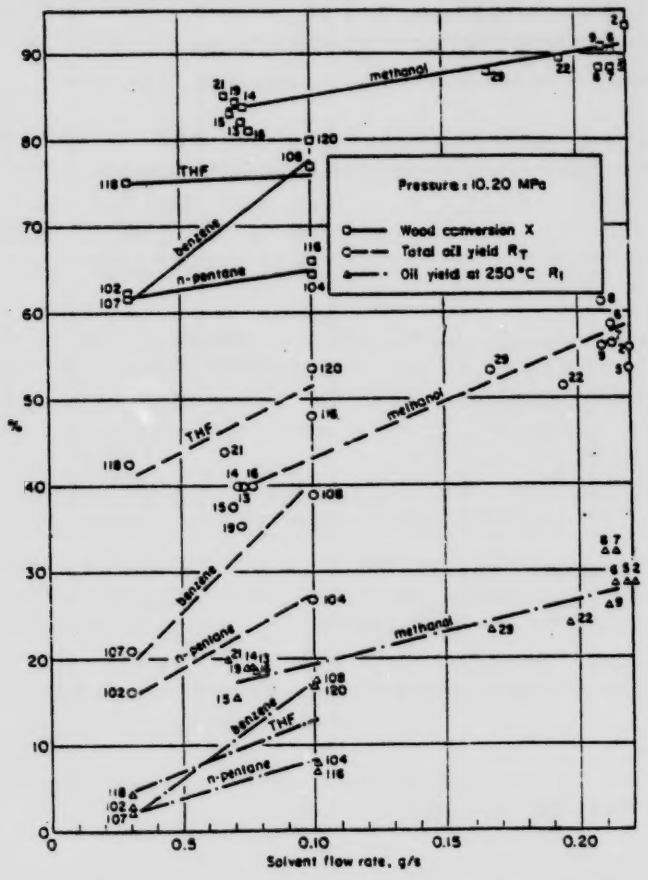

FIGURE 5. Wood Conversion and Oil Yields as Functions of Solvent Flow Rate

cases X, R_T and R_1 increase with an increase in flow rate. There are basically two kinds of physical effects which could produce such a results:

1/ for a given rate of oil production an increase in solvent flow rate means a decrease in the oil concentration in the reactor. In turn a lower oil concentration means a higher driving force for solubility and consequently a better extraction;

2/ at fixed reactor volume and solvent density, a higher flow rate means a lower residence time for the solvent and consequently a lower residence time for the oil. Therefore if some components of the oil undergo secondary reactions, the secondary conversion will increase with residence time.

We think that in the present case both phenomena are acting and that secondary reactions are of two kinds.

- With the possible exception of benzene, $X - R_T$ decreases when the flow rate increases. This means that lesser amounts of volatile compounds are formed when residence time is lower, thus secondary reactions leading to smaller molecules are less important in this case.

- With the possible exception of THF, X is an increasing function of flow rate. This would mean an increased extraction with flow rate, but we also favor the interpretation of a secondary reaction leading to secondary recondensation of molecules in solution onto the wood structure.

Indeed the char extracted at low flow rates (for example 0.075 g/s in methanol) is very much darker than the one extracted at high flow rate (for example 0.22 g/s of methanol). In these two extreme conditions BET nitrogen surface area of the char were typically found to be 11.0 and 5.3 m^2/g respectively.

The magnitude of the effect of solvent flow rate on R_T is surprisingly high. With methanol a three fold increase in flow rate produced an effect comparable to the one observed with a pressure variation from 3.40 to 17.0 MPa. We have therefore undertaken the construction of a modified version of our set-up allowing us to work at much shorter residence time.

Figure 6 shows the variations of the viscosity of oils N°2 extracted in THF at various pressures. For each oil the intrinsic viscosity was determined at three temperatures: 25, 45 and 65°C.

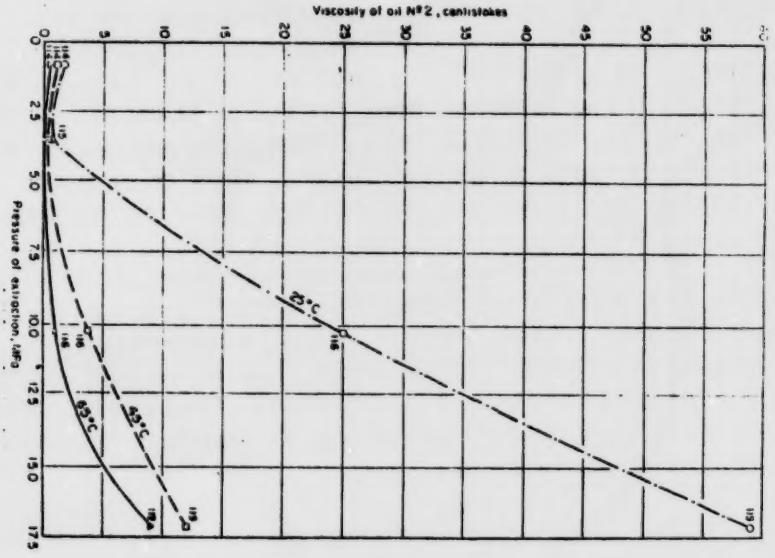

FIGURE 6. Intrinsic Viscosity of Oil N° 2 as a Function of the pressure of extraction

These results indicate a very important increase in the viscosity of oil when the pressure of extraction is raised. One possible explanation for this result would be that a higher viscosity corresponds to compounds of higher molecular sizes in the oil and therefore that at high pressure THF which is a better solvent, becomes able to extract molecular fragments of higher masses. This in turn suggests a model where pyrolysis of a long chain polymer occurs by successive rupture of bonds randomly distributed along the chain, the fragments remaining in the fibrous structure until they reach a size low enough for them to be solubilized. This model would again suppose that size reduction is much more rapid in the char structure than in the solvent.

Another possible explanation for the increase in viscosity would be an increase in molecular size by cross linking with some products of degradation of the solvent. With THF, blank experiments where the solvent has been heated in the reactor without wood, have shown the presence of traces of some compounds of degradation of THF, butyraldehyde and butyric acid. We cannot therefore exclude at that point the possibility of an addition reaction. Our chemical analysis of the oils will allow us to check for this possibility.

As already mentioned one of the interests of our experimental method is the ability to separate fractions of products formed at various temperatures. Initial evidence for this is given in Figure 7, which shows some results obtained with methanol at 10.20 MPa. When each fraction of oil is evaporated, the corresponding fraction of recondensed methanol is collected. Analysis of this methanol shows that it contains both methyl acetate and methyl formate. We presumed that these esters were produced by reaction of acetic and formic acids with hot methanol in the reactor and the calculated corresponding amounts of acids are shown as functions of time of extraction on Figure 7. As can be clearly seen from this figure, acetic acid is mostly produced during the first extraction, presumably by pyrolysis of hemicellulose, while formic acid is mainly produced during the second extraction presumably by thermal decomposition of cellulose.

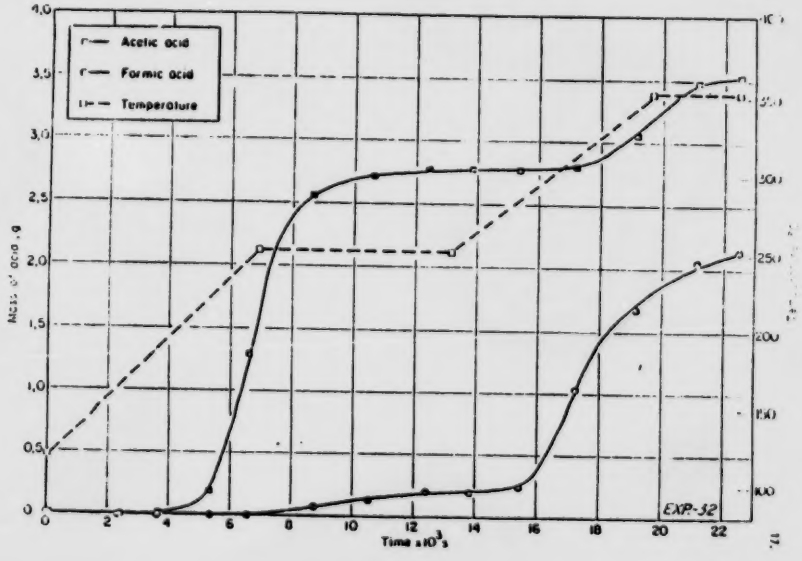

FIGURE 7. Production of Acetic and Formic Acids as a Function of Time of Extraction

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Section 4

PYROLYSIS

THE CONTINUOUS FLASH PYROLYSIS OF BIOMASS

DONALD S. SCOTT AND JAN PISKORZ
DEPARTMENT OF CHEMICAL ENGINEERING, UNIVERSITY OF WATERLOO
WATERLOO, ONTARIO, CANADA.

INTRODUCTION

In three previous publications (Scott and Piskorz, 1982a, 1982b; Scott et al, 1983) the development has been outlined of an atmospheric pressure flash pyrolysis process utilizing a fluidized bed of solid as heat carrier. The process studies had as a primary objective the determination of conditions for maximum yield of liquids from biomass, particularly forest materials. Results from a bench scale unit (15 g/h feed rate) indicated that at apparent vapour residence times of about 0.5 s, organic liquid yields of 60%-70% on a moisture free basis could be obtained from hardwoods such as Aspen-Poplar and Maple. Lower but still high yields of organic liquids could be obtained from agricultural wastes (40% - 60%) such as Wheat Straw, Corn Stover and Bagasse. Bench scale reaction conditions used a biomass particle size of -295 μm + 105μm in a nitrogen atmosphere over a temperature range of 400°C-650°C. Effects of: catalyst and lime addition; particle size, and of other reaction atmospheres (methane, and hydrogen) were also reported. In terms of calorific value and carbon to hydrogen ratio, the best quality liquid was obtained at conditions which also gave the maximum liquid yield.

In view of the high yields of organic liquids obtained - the highest yields yet reported for a pyrolysis conversion process for biomass - and the reasonable operating conditions, a larger scale continuous process unit was designed and constructed. The liquid yields attained in this unit have been as good as, or better than, those achieved in the bench scale unit, and detailed results are given in this report for three different biomass materials. A description of the process (patent applied for) is also given as well as a preliminary economic analysis.

EXPERIMENTAL

The design of the small pilot plant unit was determined in part by economic requirements for a successful biomass pyrolysis process. The outstanding economic feature

of biomass conversion processes is the costs associated with harvesting the raw material. If the biomass is available as a waste at a central facility e.g. a sawmill, then the supply will be limited. If the biomass must be harvested, this can only be done economically over a restricted distance, possibly 50 km. As a result of this limitation of supply at a site, a biomass conversion process should be economical on a small scale, so that the plant could be located at the source of raw material supply. Products from several such conversion plants could then be shipped readily to a common site for further processing, or to other customers, particularly if the products were liquid.

If a process is to be economical on a small scale it should be operationally as simple as possible, and it should require low capital investment. The pyrolysis conditions found to be optimal in the bench scale work required only moderate temperatures 450°-550°C, atmospheric pressure and the use of a fluid bed reactor. Hence, it seemed likely that the required economic criteria could be met.

The small scale pilot unit flow sheet is shown in Figure 1. Sawdust or other biomass is air dried and then

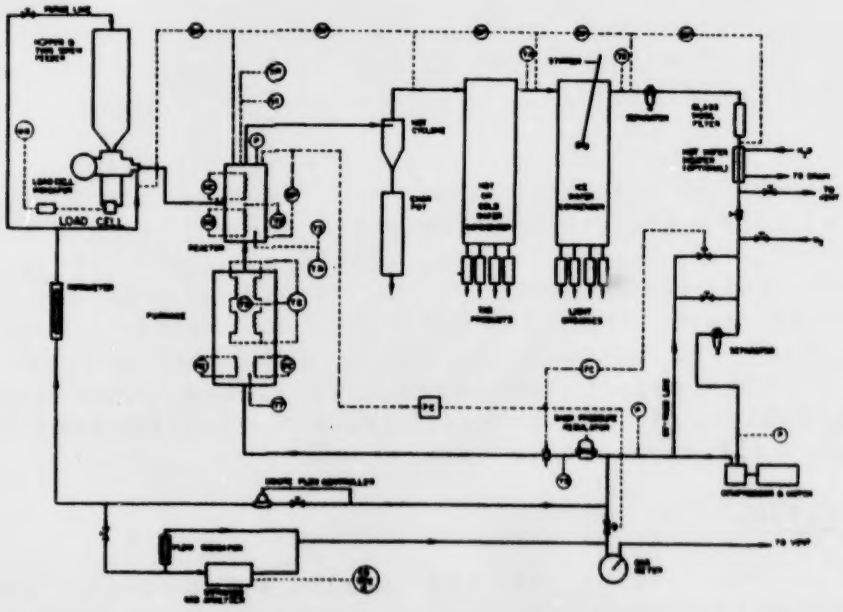

FIGURE 1. Schematic of Flash Pyrolysis Process

hammer milled and screened to -595μm (-30 mesh) particle size. The sawdust is conveyed from a hopper by a variable speed twin screw feeder, at the end of which the biomass particles are swept off the screw discharge by a flow of recycled product gas and are conveyed into the reactor. The feed injection point is within the fluid bed itself. The reactor contains sand as the fluidized material, and the fluidizing gas is recycled product gas which has been preheated in the inlet line by controlled electric heaters. In addition, the reactor is wrapped with heating coils allowing extra heat to be added either to the bed of sand or to the freeboard space as desired.

Pyrolysis products are swept from the reactor to a cyclone, together with all the char formed. The char is separated in the cyclone and the product gas and vapours pass to two condensers in series. These condensers have the pyrolysis gas inside the tubes, which are vertical. Every tube has a clean-out plug at the top and a condensate collection pot at the bottom. The first condenser can be operated at temperatures up to 100°C, while the second condenser uses chilled water at 0°C as a cooling medium. The gas from the condensers then pass through a series of filters to remove tar mist and then to a recycle compressor. A regulated gas flow is taken from the compressor discharge to fluidize the reactor and to convey feed into the reactor, while the excess is vented through a gas analyzer and gas meter as product gas.

The method of operation of the fluidized bed reactor is unique to this process. Existing fluid bed pyrolysis technology normally uses twin fluid beds, in the first of which pyrolysis occurs. The sand and char are then circulated to a second fluid bed where the char is burned and the sand heated. The hot sand is then returned to the first bed to supply the required heat of reaction. While this method of pyrolysis is used commercially e.g. for municipal waste gasifiers it can have operating problems with transfer lines, and is expensive. In our reactor, the design has been carried out so that during pyrolysis the char formed is blown from the bed and the sand is retained in the bed. By carefully selecting sand size, biomass particle size, bed velocity and reactor configuration this method of operation can readily be successfully achieved. This "blow-through" method of operation has been used without problems under a variety of conditions in the continuous unit described here.

After tests in which biomass equal to several times the weight of sand in the bed had been fed, it was found that the bed contained a negligible amount of char. The outcome of this special design and mode of operation is that only a single fluid bed is required with consequent savings in capital costs and reduction in operational problems, inasmuch as no sand circulation or replacement is necessary. Further, the heat of reaction for biomass pyrolysis carried only to the point of producing a high proportion of liquid products is small, and may be either slightly endothermic or exothermic depending on the biomass species. As a result, relatively little heat needs to be added to the reactor, and this can generally be readily accomplished by heating the fluidizing gas to somewhat above the reaction temperature.

A drawing of the pilot plant reactor is shown in Figure 2. In the present work a cylindrical reactor was

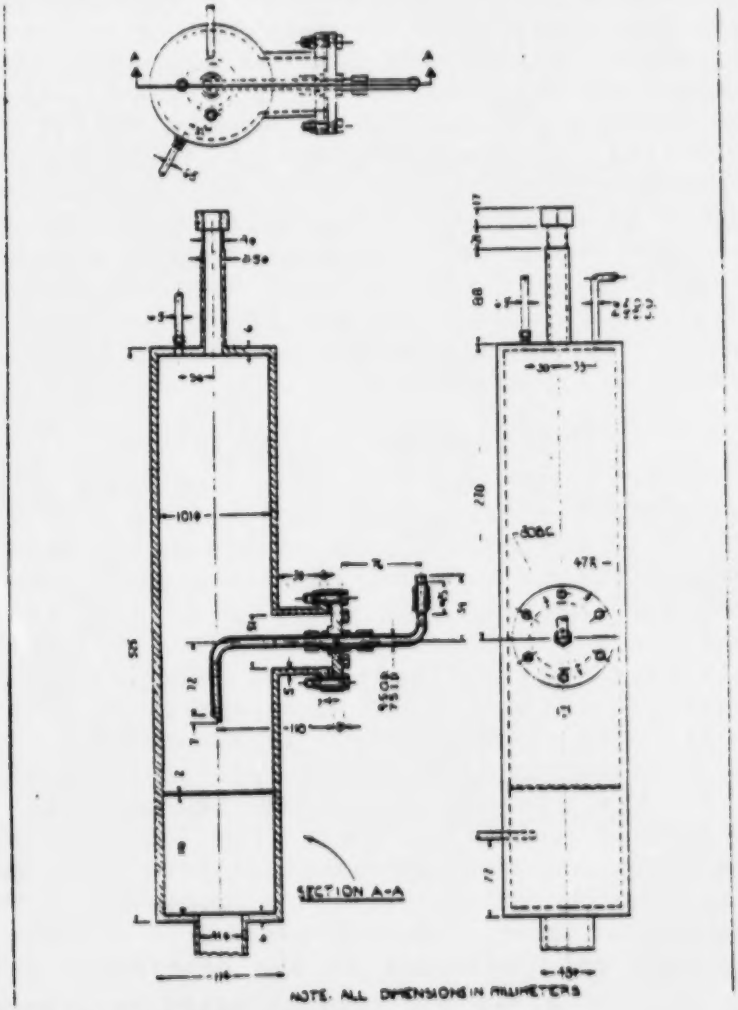

FIGURE 2. Details of Fluid Bed Reactor

used, but there are potential advantages in using other configurations. The residence times in the reactor are difficult to define. In this work, the residence time is calculated as an apparant gas residence time, based on the volumetric flow rate of the total fluidizing gas at reactor conditions and the net empty reactor volume. In fact, actual vapour residence time will be less than this, because of the vapour volume generated in pyrolysis. This extra volume flow would reduce the apparent vapour residence time by about 15% on the average. Char residence time is not known with any certainty, but the small char accumulation in the bed at any time suggests that it would be only slightly longer than that of the vapour.

Temperatures and pressures were monitored throughout the unit, the former by means of thermocouples, and the latter by differential and absolute bellows type gauges. The feed hopper and feeder were mounted on a hinged platform resting on a load cell, and hopper weight loss was continuously recorded. Reaction temperature was controlled by a thermocouple in the fluid bed which regulated the inlet gas heating coils.

Normally, a run was started by bringing the reactor to temperature with total recycle and nitrogen flowing in the system. After reaching a suitable temperature level, biomass feed was started (from 1.5 - 3.0 kg/h) and within about 10 minutes the system had reached a final steady state with respect to both temperature and gas composition (system volume was small, so total system residence time was about 10 seconds). Run time varied from 45 minutes to 120 minutes, and temperatures for 425°-625°C. Reactor pressure was usually about 125 kPa absolute.

No chronic problems were encountered with the pilot unit except for the need to remove all of the tar aerosols which form readily in the condensers in order not to affect compressor operation. The amount and nature of the tar aerosol formed depends on the type of cooling used. In this unit, with surface condensers - used to allow complete material balances to be carried out - a considerable amount of stable aerosol formed, the amount of which also depended on the type of biomass. It is probable that liquid direct contact scrubbers might be preferable in larger scale operations.

ANALYSIS OF PRODUCTS

In general, four products were recovered after a run. From the two condensers a fairly fluid oil was obtained which also contained most of the water produced. This "liquor" fraction varied from about 50% of the total liquid yield for wheat straw to about 85% for the poplar-aspen and maple. It was a dark fluid, with an acrid smell, easily pourable and showing only one phase. It contained from 15% - 30% water depending on the type of feed and its moisture content. This oil appeared to be stable on the shelf over periods of weeks if not exposed to air.

After a run, the condensers were washed with acetone, the solution filtered, and the acetone subsequently evaporated under vacuum to yield a "tar" fraction. Additional tar was collected in the filters which were also weighed before and after a run. If the tar amount in the filters was substantial, which was the case only at the highest temperatures or for wheat straw feed, the filters were also washed with acetone and the tar recovered. All liquid products were readily soluble in acetone.

Char was collected from the char pot and weighed. This char was very reactive and precautions were required to ensure that it did not react with air when hot. The residue from the filtration of the tar fraction, that is, any acetone insoluble material recovered, was also included in the char fraction.

Gases were analyzed for CO and CO_2 in an on-line infra-red gas analyzer-recorder. Samples of the product gas were also taken periodically and analyzed by gas chromatography.

Biomass fed was obtained not only from the weight loss recorder, but was checked by independent weighing of the feed hopper contents before and after a run. Elemental analyses of feed and products was done using a Perkin-Elmer 240C elemental analyzer. Water content of liquid products was determined by Karl Fischer titration.

RESULTS AND DISCUSSION

The feed used in all cases, unless otherwise specified, was -595μm, (-30 mesh) in size. No fines were removed from the feed, so a rather wide range of particle sizes resulted. Particles from wood were primarily cylindrical, with the largest diameter approaching 595μm, but the length often four or five times that value. Screen analyses of the four feeds used are given in Table 1. Although the aspen-poplar gave a considerable amount of fines (-88μm), the fines produced by the wheat straw were much smaller, and the latter had a significant amount of "dust", which was not noticeable with the wood feed material.

Table 1. Particle size analysis

Mesh Size	Sieve Size,μm	Maple	IEA Aspen	Brockville Aspen	Wheat Straw
			% by weight		
+30	+595	0	0	0.13	0
-30+50	-595+300	57.40	30.16	30.19	27.42
-50+60	-300+250	21.68	17.81	16.46	19.54
-60+100	-250+149	14.29	22.96	24.06	25.67
-100+140	-149+105	2.35	10.02	10.66	11.18
-140+170	-105+88	1.33	1.52	1.59	1.92
-170	-88	2.96	17.51	16.91	14.29

Initial pilot plant runs were carried out using maple mill waste hammer milled to -595μm. Results are shown in Table 2 and indicate the high yields obtainable from the flash pyrolysis of hardwoods. During the course of these

Table 2. Pilot Plant Results

Maple - 7% Moisture, -595μm, 0.59% Ash, 48.5% C, 6.1% H, 0.50% N(MF)

Preliminary Tests

Run No.	8	9	4	2
Bed Temp. °C	518	532	530	530
Feed Rate kg/hr	2.827	2.191	2.788	1.773
Yields, % MF				
Org. Liquids	68.24	66.89	58.39	61.83
H_2O (by G.C.)	10.6	9.7	8.6	9.8
Char	13.25	9.37	17.85	14.73
Gas	9.98	10.02	7.27	7.96
H_2	.043	.043	.011	--
CO	5.05	5.78	2.48	3.96
CO_2	4.48	3.68	4.53	3.98
CH_4	.24	.61	.14	--
C_2H_4	.15	.20	.06	--
C_2H_6,C_3's	.022	.037	.046	--

runs, two observed effects led to modifications in the process. The reactor was heated only by the incoming gas, and temperature measurements in the bed and at the reactor outlet showed a significant drop in reactor wall temperature from the bed to the exit. This appeared to be only partly due to heat loss, and indications were that endothermic reactions were continuing in the freeboard space. As a result, external coil heaters were added to the reactor, so that heat could be added to the bed or to the freeboard separately if desired. Since the bench scale reactor was operated isothermally, the pilot unit might compare best if also operated isothermally. A second problem arose due to the formation of stable tar aerosols which passed readily through the condensers. Special packing in the condenser tubes largely controlled this problem for hardwoods, and in subsequent runs the packed tubes were used as well as oversized filters following the condensers.

Table 3 and Figures 3 and 4 show the results for organic liquid, char and gas yields from pyrolysis of maple sawdust under both adiabatic and isothermal conditions, compared to bench scale results. The scale up is by a factor of 100, so the agreement in results is quite gratifying. In general, organic liquid yields above 500°C were about the same or higher than those from the bench scale unit, despite

Table 3. Pilot Plant Results

Maple, 3.8% moisture, -595μm, 0.59% Ash, 48.5%C, 6.1%H, 0.50%N (mf)

Run No.	13	16*	12	11*	14	9	17*
Bed Temp. °C	482	480	500	500	532	531	530
Feed Rate kg/hr	2.608	2.169	2.678	2.573	2.158	2.118	2.594
Yields, %m.f.							
Org. Liquids	60.63	66.54	64.68	64.16	67.25	69.54	61.21
H_2O (by K.F.)	6.3	6.9	8.2	8.9	7.4	7.8	8.2
Char	20.90	12.41	12.61	9.24	9.02	9.37	10.32
Gas	8.42	10.51	10.27	12.31	12.05	10.35	16.51
	96.25	96.36	95.76	94.61	95.72	97.06	96.24
H_2	.016	.036	.037	.055	.045	.037	.122
CO	3.93	5.25	5.16	7.25	6.96	5.78	10.37
CO_2	4.05	4.27	4.48	3.91	4.02	3.67	4.47
CH_4	.29	.62	.44	.83	.75	.61	1.22
C_2H_4	.11	.24	.15	.25	.24	.21	.27
C_2H_6,C_3's	.018	.080	.022	.026	.038	.036	.044
Gas Composition, % by volume							
H_2	3.24	4.93	5.87	6.23	5.28	5.30	9.76
CO	47.8	54.5	57.8	59.6	59.7	58.4	60.1
CO_2	39.1	27.3	26.2	20.2	21.7	23.4	16.3
CH_4	7.89	10.39	8.41	11.78	11.18	10.46	12.13
C_2H_4	1.69	2.29	1.59	1.99	1.96	2.03	1.50
C_2H_6	0.21	0.30	0.13	0.17	.18	0.19	0.13
C_3+	.03	0.28	0.07	0.02	.09	0.11	0.06

*Isothermal Runs

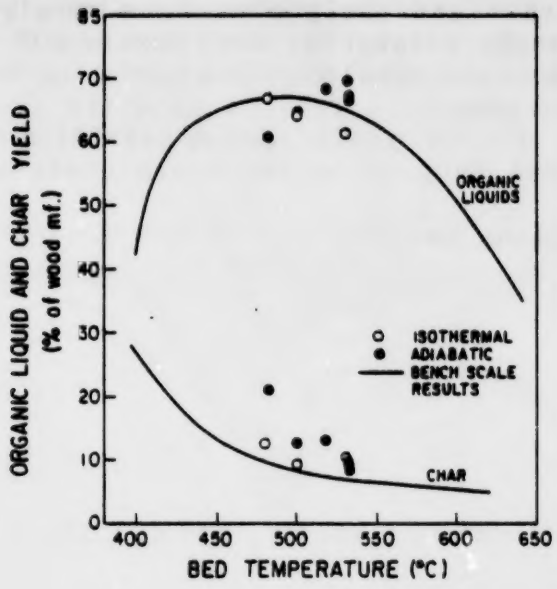

FIGURE 3. Organic Liquid and Char Yields from Maple mill Waste Comparison with Bench Scale Operation

two major differences in pyrolysis conditions. The pilot unit used -595μm particles with sizes down to 88μm or less, while bench scale work was done with -250 + 105μm particles. Secondly bench scale results were obtained in a nitrogen atmosphere, while the pilot unit operated using recycle gas with the composition shown in Table 3, that is, about 48% - 60%CO, 16% - 40%CO_2, and 8% - 12% CH_4. It appears that in the temperature range of 450° -550°C, neither particle size nor reaction atmosphere is a major influence on organic liquid yields, which is in agreement with findings from bench scale work.

Figures 3, 4 and 5 show that isothermal operation

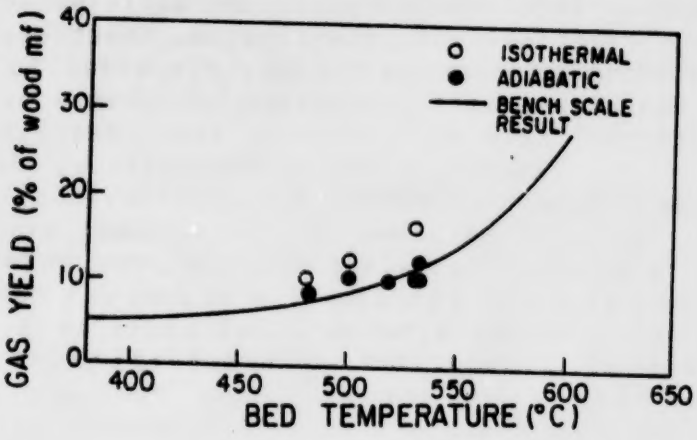

FIGURE 4. Gas Yields from Maple Mill Waste Comparison with Bench Scale Operation

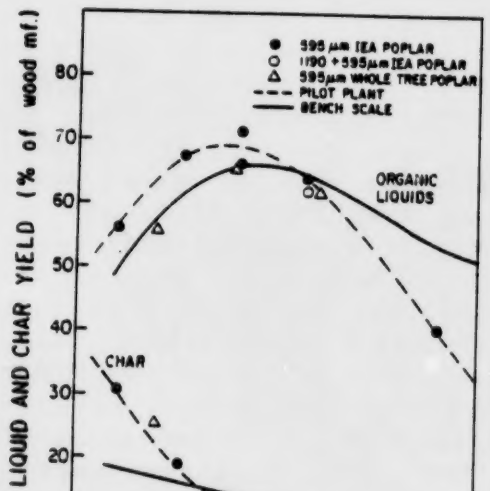

FIGURE 5. Organic Liquid and Char Yields from IEA and Whole Tree Poplar-Aspen wood Comparison with Bench Scale

gives reduced liquid yields at higher temperature, reduced char yields and higher gas yield as compared to adiabatic operation. This result would be anticipated if secondary cracking reactions of the liquid fraction, and further decomposition of char particles, proceeded in the freeboard area. The higher wall temperature and extra heat transfer in the isothermal case would promote these reactions, leading to the observed results. As a consequence, further reactor operation was carried out entirely adiabatically.

Organic liquid and char yields for the pyrolysis of hybrid poplar-aspen are shown in Figure 5, and gas yields in Figure 6. The two feed materials used were from the same experimental plantation at Brockville Ontario (Ontario

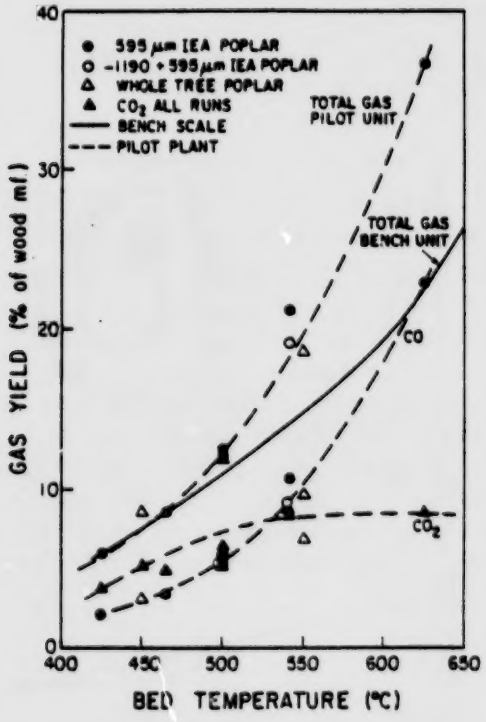

FIGURE 6. Gas Yields from IEA and Whole Tree Poplar-Aspen Wood Comparison with Bench Scale

Ministry of Natural Resources, Populus canescens, 8 years old, Clone C-147) the wood sample being a clean bark free standard lot received from International Energy Agency (see Beckman these proceedings page 4), with the "whole tree" sample being obtained from six whole trees, including bark and branches. This latter material was estimated to contain 15%-20% bark.

Yields of organic liquids from both the clean wood and the whole tree material show very similar values, with the clean wood giving slightly higher maximum yields (about 69% vs 66% of the moisture free wood). The trends and yields of organic liquids follow closely the same trends that were observed in the bench scale unit, although the yield of liquids is somewhat higher in the pilot plant unit. One test was also carried out using the clean wood and a particle size of -1190 to +595μm. The yields of organic liquids, gas and char are very similar to those obtained with the -595μm feeds in the pilot plant or the -250 + 105μm feed used in the bench scale apparatus.

Figure 6 shows the yields of CO and CO_2 produced by pyrolysis in the pilot plant, as well as the total gas yield. At temperatures above 550° there is a considerably larger gas yield from the pilot plant than that obtained in bench scale work under an N_2 atmosphere. This higher gas yield at higher temperatures corresponds to the more rapid falling of in liquid yield for the pilot plant runs as shown in Figure 5. It may be concluded that relatively little additional primary pyrolysis occurs in the fluid bed of the larger reactor, since char yields in pilot plant and bench scale units are similar at higher temperatures. Therefore, the extra gas formed and the reduced liquid yield in the pilot plant at higher temperatures represent secondary decomposition reactions likely occurring in the free-board space. However, at the optimal temperature of about 500°C, these secondary reactions appear to be minimized.

The gas produced is a medium quality gas with a higher heating value of about 14.4 MJ/std.m^3 for the composition obtained at 500°C. This heating value increases at higher pyrolysis temperatures as CH_4 content increases and CO_2 content decreases.

Detailed results for the pyrolysis of the poplar-aspen wood (IEA sample) and the whole tree wood (Brockville sample) are given in Tables 4 and 5. Table 6 gives the analysis of some volatile liquid components recovered in the aqueous condensate fraction for runs using the whole tree wood. Acetic and propionic acids form the largest part, with acetic acid being two to three times as large as all other components combined. It is possible that what is reported as HAc is actually 2 or 3 separate components not separated by our G.C. From 6%-7% of the dry wood appears as acetic acid, and this component would probably be recoverable as a single product.

Table 4. Pilot Plant Test Results

IEA Standard Poplar-Aspen, -595um, 6.25% moisture, 0.44% Ash m.f.
C (mf) 48.39%, H (mf) 5.89%, N = .068%

Run No.	30	28	27	29	25	26	34*
Vapor Res. Time, secs	0.616	0.584	0.550	0.550	0.539	0.520	0.539
Temp. in Bed, °C	425	465	500	500	541	625	541
Feed Rate, kg/hr	2.391	1.709	2.238	1.970	1.281	1.001	1.297
Yields, % of Wood mf.							
Organic Liquids	55.88	67.17	65.75	71.15	63.65	40.27	62.05
Water (K.F.)	3.8	5.5	9.3	6.6	7.4	4.1	7.7
Char	30.51	18.88	12.15	11.20	8.99	7.81	9.72
Gas	5.95	8.53	12.45	12.07	21.22	36.65	19.11
H_2	.004	.009	.019	----	.064	.235	.043
CO	2.06	3.27	5.32	5.39	10.47	22.88	9.13
CO_2	3.72	4.86	6.30	5.86	8.64	8.44	8.25
CH_4	.091	.20	.48	----	1.28	3.51	.89
C_2H_4	.038	.085	.20	----	.49	1.09	.36
C_2H_6	.010	.021	.043	----	.12	.23	.15
C_3+	.031	.085	.085	----	.16	.27	.31
Overall Recovery, %	96.14	100.08	99.66	101.02	101.26	88.83	98.58
Liquid Condensate, gms/ml	1.145	1.171	1.172	1.200	1.130	0.992	1.158
% Water in Condensate	25.7	21.5	24.8	20.9	26.6	41.8	23.31
Char Analysis, %							
C	55.13	59.28	66.77	----	69.99	73.16	72.45
H	5.48	5.25	3.90	----	2.80	2.33	6.49
N	---	-----	.35	----	.30	.43	.26
Ash	3.4	2.01	3.2	----	6.5	9.5	6.57
Condensate (incl. H_2O)							
C							37.42
H							4.52
% Yield of Wood	35.13	41.12	49.12	52.91	42.65	24.2	49.15
Tar Washings (solvent removed, moisture free)							
C	53.36	56.61	57.30	---	57.88	56.59	55.29
H	5.69	6.18	6.29	---	6.22	6.34	5.78
% Yield of Wood	26.30	30.69	24.72	24.86	28.36	37.8	20.48

* -1190+595_m

Table 5. Pilot Plant Results

Hybrid Poplar - Aspen - Whole Tree (Brockville)
-595um, 6.26% moisture, 1.26% Ash (mf) C= 46.91, H=5.62, N=1.08 (mf)

Run No.	33	31	32
Vapor Res. Time secs.	0.689	0.600	0.555
Temp. in Bed °C	450	500	550
Feed Rate, kg/hr	1.683	1.339	1.462
Yield, % of Wood mf			
Organic Liquids	55.82	65.78	61.96
Water (K.F.)	5.30	4.3	5.3
Char	25.46	13.21	10.64
Gas	8.57	11.85	18.56
H_2	.01	.019	.043
CO	3.02	5.25	9.57
CO_2	5.18	5.74	6.89
CH_4	.20	.45	1.14
C_2H_4	.10	.23	.49
C_2H_6	.017	.053	.16
C_3+	.035	.12	.28
Overall Recovery, %	95.15	95.14	96.46
Liquid Condensate, gms/ml	1.120	1.172	1.121
% Water in Condensate	22.8	30.1	25.5
Char Analysis, %			
C	53.84	60.22	59.77
H	4.83	2.97	2.81
N	--	1.07	0.17
Ash	3.89	7.16	10.30
Condensate (incl H_2O)			
C	38.32	31.65	35.80
H	5.06	4.46	4.84
% Yield of Wood as fed	42.56	34.13	43.85
Tar Washings (solvent removed, mf)			
C	50.33	51.90	52.00
H	5.58	6.43	6.22
% Yield of Wood as fed	20.97	37.79	25.41

Table 6. Pilot Plant Results

Hybrid Poplar - Aspen, Whole Tree (Brockville)
-595um, 6.26% moisture, 1.26% ash mf.
Light Organics in Condensate Fraction

Run No.	33	31	32
Condensate Yield, % of wood as fed	42.56	34.13	43.85
% Water in Condensate (K.F.)	22.8	30.1	25.5
Temp. of Bed °C	450	500	550
Yields, % by weight condensate			
Methanol	0.91	1.06	1.15
Furan, Acrolein	2.13	1.11	0.95
Acetic Acid	14.52	18.81	13.38
Propionic Acid	2.76	3.81	3.08
Furfural	0.60	0.59	Trace
Acetic Acid, % wood m.f.	6.84	6.59	6.26

The aqueous condensate plus tar fraction from maple or poplar-aspen pyrolysis when combined give a dark liquid with an acrid smell. The liquid has a single phase (water is dissolved in the organic phase) and will contain 10%-20% water, depending on moisture content of the feed and the pyrolysis temperature. The mixed liquid product is fluid and pours readily, and has a viscosity of about 40 cp at 40°C (Elliott, 1983). The liquid has a density of about 1200 kg/m^3 and a pH of 2.3-2.8. It contains about 35-40% oxygen, with the minimum oxygen content occuring at the conditions of maximum liquid yield.

Tables 7 and 8 show the carbon and hydrogen contents of the chars and organic liquids produced. The char

Table 7. C-H Balances IEA Poplar - Aspen, 48.39%C 5.89%H (mf), 0.44% ash -595µm.

Run No.	30	28	27 29	25	26	34*
Temp. °C	425	465	500	541	525	541
Elemental Analysis :						
Char C	55.13	59.28	66.45	59.99	73.16	72.45
H	5.48	5.25	4.43	2.80	2.33	2.87
Org. Liquid C	53.36	56.61	55.15	57.38	56.59	55.29
H	5.69	6.10	6.1	6.24	6.34	6.20
C Recovery :	92.1	98.6	97.5	99.9	86.4	94.7
C Normalized :	95.8	98.5	--	98.6	96.5	96.0
H Recovery :	96.4	103.2	94.3	101.0	84.1	95.2
H Normalized :	100.3	103.1	--	99.7	93.9	96.5
H/C molar ratio, liquid	1.28	1.31	1.33	1.31	1.34	1.25
H/C molar ratio, char.	1.19	1.05	.80	.48	.38	.48
C Conversion to liquids, norml	60.1	59.5	77.6	63.2	49.7	67.4

* -1190+595µm

Table 8. C-H Balances, Brockville Poplar Aspen, 46.81%C, 5.62%H, 1.26% Ash (mf) -595µm

Run No.	33	31	32
Temp. °C	450	500	550
Elemental Analysis, %			
Char. C	53.84	60.22	59.77
H	4.83	2.97	2.81
Organic Liquid C	50.88	51.90	52.00
H	5.65	6.43	6.22
C Recovery %	90.3	93.9	92.5
C Normalized %	94.6	98.4	95.7
H Recovery %	96.6	100.4	99.1
H Normalized %	101.2	105.2	102.5
H/C molar ratio,liquid	1.33	1.49	1.44
H/C molar ratio,char.	1.08	0.59	0.56
C conversion to liquids (Norm)	59.6	71.6	66.7

HHV (approx.)

from clean wood (Table 6) shows a steady increase in carbon content and decrease in hydrogen content with temperature, with the H/C molar ratio falling from 1.19 at 425°C to 0.38 at 625°C. The H/C ratio for the organic liquid appears to be approximately constant at about 1.3 over the range of 425°C-625°C. It is interesting that the compositions of the char and organic liquids from the large sized particles (Run 34) in which no fines were present, are essentially the same at the same temperature as the products obtained from the smaller particles with a wide range of particle sizes.

Table 9 shows the results of pilot plant runs using

Table 9. Pilot Plant Results - Wheat Straw -595μm, 5.3% moisture, 3.8% ash mf, C=44.16% H.5.70%

Run No.	20	22	23	19	21	24
Vapour Res. Time, secs	0.75	0.60	0.54	0.57	0.71	0.52
Bed. Temp °C	500	500	520	525	550	575
Feed Rate, kg/hr	1.919	1.717	1.114	2.762	1.509	1.587
Yields, % of wood, mf.						
Organic Liquids	43.04	48.87	57.06	44.98	36.27	47.61
Water	13.22	2.81	4.76	8.66	7.20	3.92
Char	23.66	20.60	16.85	24.17	19.13	17.30
Gas	18.92	13.61	15.67	8.63	23.88	23.24
H_2	.022	.011	.037	.008	.052	.13
CO	6.91	4.74	6.34	3.03	10.57	11.08
CO_2	10.72	8.26	8.10	5.26	10.75	9.33
CH_4	.74	.32	.77	.21	1.34	1.83
C_2H_4	.20	.11	.31	.070	.42	.68
C_2H_6	.13	.044	.041	.025	.022	.082
C_3+	.22	.15	.074	.026	.053	.12
Overall Recovery %	98.84	85.89	94.34	86.44	86.48	92.07
pH of Liquid	3.41	3.12	3.49	3.12	3.64	3.83
Char Analysis %						
C	57.26	--	57.77	--	--	55.01
H	3.17	--	2.63	--	--	2.10
Ash	19.07	--	22.65	--	--	21.19
Tar Analysis %						
C	55.55	--	56.04	--	--	56.85
H	6.39	--	6.61	--	--	6.75
C Recovery %	94.7	--	98.4	--	--	102.0
H Recovery %	98.6	--	88.8	--	--	94.0

-595 m wheat straw and in Figure 7 these results are shown compared to those from bench scale work. Despite the scatter

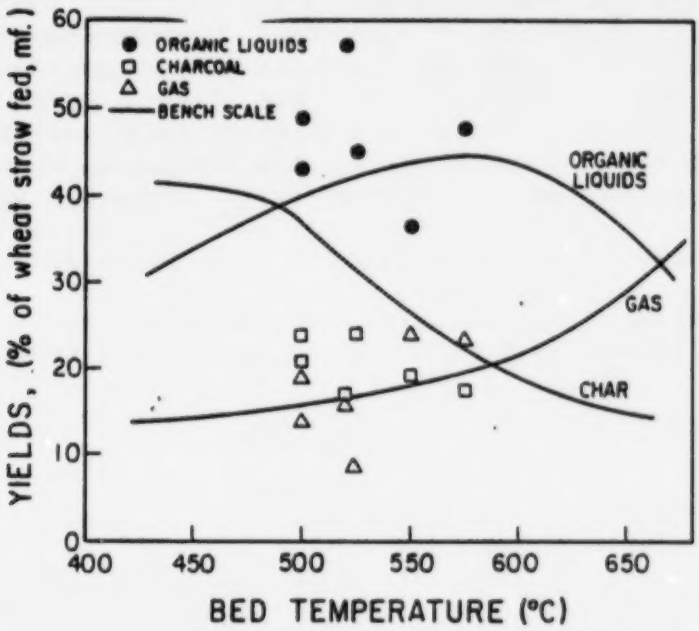

FIGURE 7. Yields of Liquid, Char and Gas from Wheat Straw comparison with Bench Scale Results

in the results from the pilot plant tests, the two are in general agreement. Maximum liquid yields appear to occur at somewhat lower temperatures in the pilot unit, and char yields appear to be less at lower temperatures. However, the considerable amount of very fine dust in the pilot plant feed undoubtedly causes some error in the relative amounts of tar and char reported. The combined oil and tar from the wheat straw was more fluid and had a significantly higher pH of 3.2 to 3.8 than did the wood oil. Organic liquid yields were lower and char yields higher from wheat straw than from wood, in agreement with bench scale results. Tar elemental analyses are very similar for wheat straw and wood. The char, however, has a lower C content from the wheat straw and much higher ash content.

The similar results obtained for the poplar-aspen wood of widely different particles sizes suggest that the pyrolysis is proceeding by what has been termed an "ablative pyrolysis" (Diebold, 1980). An approximate heat transfer model was employed to obtain some concept of the heat transfer behaviour in the pilot plant reactor shown in Figure 2. The heat transfer equations were solved for the heating up of the wood particles in the injection tube. The heat transfer in the fluid bed and in the transport section in the freeboard was approximated by assuming the minimum Nusselt number of 2, or a somewhat higher value of 4.
Results for 100μm, 595μm and 1000μm particles are shown in Figure 8, for a reactor temperature of 500° in which the outside surface temperature of the particle is plotted against the time from the point of discharge from the screw conveyor. If particles are less than about 200μm, the surface temperature reaches the reaction temperature in less than 0.5 seconds. Since internal temperature gradients are not large, the temperature at the particle centre will be only a little less. However, for 595μm particles or larger at the 0.5 -1.0 seconds residence time which was the probable range in the pilot plant reactor for the solid particles, the outer surface temperature never attains the reaction temperature. Hence, the high liquid yields obtained are probably due to the fact that the initial cellulose - hemicellulose - lignin decomposition reactions occur at relatively low temperatures to yield liquid products (tar),

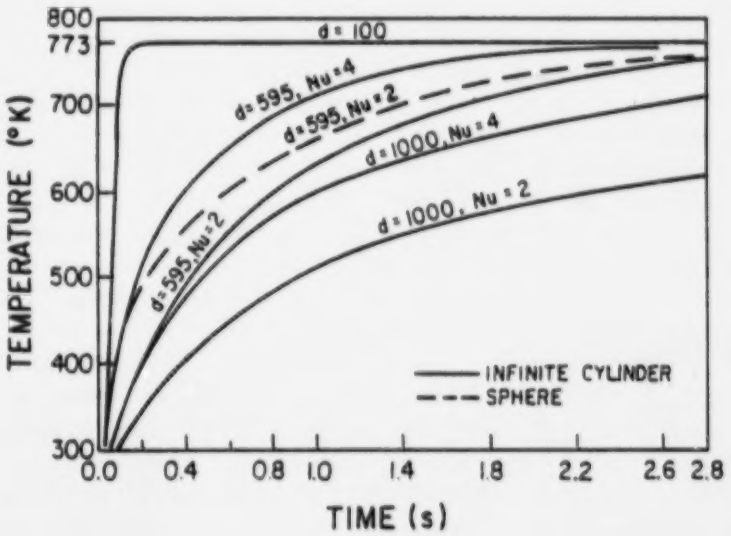

FIGURE 8. Approximate Outside Surfacr Temperatures of Biomass Particles during Pyrolysis

and these escape readily from the particle since they form at the outer surface of the unreacted wood. The short vapour residence time allows these liquids to be swept from the reactor with relatively minor secondary decomposition occurring. As the great bulk of the mass of wood reacting is in the larger particles, the somewhat lower surface temperatures attained by these larger particles may account for the somewhat higher liquid yields observed with larger particles in the pilot plant relative to bench scale results. Further, adiabatic operation in which the upper part of the reactor is somewhat cooler than the fluid bed would also be expected to give somewhat better liquid yields, particularly at higher temperatures, as was observed.

The development of processes based on the thermal pyrolysis of biomass have been directed largely to gasification, either for fuel gas or synthesis gas production, and many such processes have been described. The pyrolysis of biomass to give a maximum direct yield of liquid products has received much less attention, and very few studies have been reported, for example, Duncan et al (1981) Kosstrin (1980), Roy et al (1982), Scott and Piskorz (1983). Of these, only work of Kosstrin, and Scott and Piskorz, appears to have both used a fluid bed reactor and been directed to maximizing liquid yields. Roy et al pyrolysed batch - wise under vacuum, and Duncan et al (hyflex process) used a transport reactor under pressure. Comparison of the results reported here with those of other workers, whether using fluid bed reactors or other types shows that as high or higher organic liquid yields have been achieved in this work. Although there is an extensive literature on the mechanisms of biomass pyrolysis reactions, until the heat and mass transfer behaviour in a particular reactor are understood, it is difficult to speculate on why liquid yields may be better in one process than another. In the case of the fluidized bed reactor, this analysis is presently underway in our laboratories.

ECONOMIC ANALYSIS

A preliminary economic analysis has been carried out for a plant processing 1000 t/day (dry basis) of waste wood. The analysis was based on a conceptual flow sheet derived from Figure 1, but using scrubbers to recover liquid products, rather than condensers. Heat for the reaction was assumed to be supplied by burning the char and a portion of

the product gas. Heat recovery from the scrubbers and char burner was practised and the waste heat used for the drying of the wood chip feed, assumed to be 40% moisture. The liquid product was not further treated or separated from the scrubbing liquid in this analysis, as the scrubbing liquid was assumed to be a product fraction.

The total capital cost (fixed plus working capital) was estimated to be $33.8 million, and the total annual production cost, excluding raw material cost, for the process was $55.20/tonne of organic liquid (water free), based on 330 days/year of operation and a 10 year plant life, without credit for unused fuel gas. Allowing a credit for this gas, and assuming a heating value of 19.88 MJ/kg for the organic liquid, an energy cost, exclusive of raw material cost, of 2.0$/GJ is obtained ($2.11 per million BTU). To this must be added the cost of the green waste wood chips. At about $30 per dry tonne, the production cost would be about double the above figure. The total energy efficiency defined as useful output energy referred to all energy inputs (raw material plus utilities) is 68% - 70%.

It can be concluded that for a large scale plant, the proposed flash pyrolysis process could produce a liquid fuel which might be competitive at the present time in the right circumstances with fuel oil. If a much smaller plant is contemplated, e.g. 100 dry tonnes/day the energy production cost is estimated to be about 30% higher.

SUMMARY

A continuous atmospheric pressure flash pyrolysis process for the production of liquids from biomass has been demonstrated on a scale of 2-3 kg/hr. Yields from harwoods (maple or hybrid poplar-aspen) as high as 65 - 70% of the dry wood fed can be achieved at optimal conditions. At the optimal conditions, the organic liquid produced shows a minimum oxygen content also, although this is still relatively high (35%). Hydrogen/carbon ratio of the char decreases steadily as temperature increases while that of the liquid remains relatively constant. Gas produced has a medium heating value of around 14 MJ/std.m^3. Wheat straw gives significantly lower liquid yields than hardwoods (45-50%) with higher optimal temperature. The liquid product obtained appears to differ significantly also from that obtained from wood.

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OIL PRODUCTION BY ENTRAINED FLOW PYROLYSIS OF BIOMASS

J.A. KNIGHT AND C.W. GORTON

ENGINEERING EXPERIMENT STATION
GEORGIA INSTITUTE OF TECHNOLOGY
A UNIT OF THE UNIVERSITY SYSTEM OF GEORGIA
ATLANTA, GEORGIA 30332

INTRODUCTION

Wood pyrolysis oil is a versatile product and has been used successfully as a fuel for commercial kiln operation and in the operation of a power boiler (Bowen, M.D., et al, 1978). According to Bowen et al, wood pyrolysis oil was also tested by Trane Thermal in their vortex burner and by KVB in a test boiler. Both of these tests were successful. The oil has been blended and test burned successfully with pulverized char and/or other fuel oils (Bowen, M.D., et al, 1978, Demeter, J.J., et al, 1977). Thus, pyrolysis oil from wood has been demonstrated to be an acceptable liquid fuel in commercial applications. Wood pyrolysis oil has been tested as an alternate fuel for gas turbines, and the results indicate that the process is technically viable with high combustion efficiency (Jasas, G. & J. Kasper, 1982). Wood pyrolysis oil has potential as a chemical feedstock. Properties of wood pyrolysis oil obtained from a 50 dry ton/day field development unit have been reported (Knight, J.A. et al, 1977).

Because of the need for liquid fuels and the demonstrated utilization and favorable characteristics of wood pyrolysis oil as a fuel, the research effort at Georgia Tech is currently emphasizing the production of oil and is seeking to determine the conditions for maximum oil production by entrained pyrolysis of wood. Recent research efforts at Georgia Tech utilizing a small rotating tube furnace have demonstrated increased oil yields as compared to stationary tube furnace results. The rotating tube furnace yields are typically about 28% by weight of original dry feed (Knight, J.A. et al, 1981) as contrasted to 17% for the stationary tube furnace yield (Knight, J.A., 1976). This is believed to be attributed to the "showering" of the wood particles through the gases in the tube furnace as opposed to

the "packed-bed" mode of the stationary tube furnace. A recent publication (Kosstrin, H., 1980) based on experimental data indicated that the pyrolysis of sawdust in a fluidized bed gives oil yields as high as 36%. A mathematical model of the process, which predicts the data trends well, was based on postulated kinetics which includes oil formation and subsequent decomposition of the oil to char and gases so that a maximum is exhibited in the oil production rate (Kosstrin, H., 1980). Recently, Scott and Piskorz (Scott, D.S. & J. Piskorz, 1981) reported yields as high as 62% pyrolysis oil and 4% organic liquid by weight of dry wood feed. The ground wood particles were conveyed into a fluidized bed of sand.

A pyrolysis system operating in the entrained mode has the advantages given in Table 1. The high throughput is a characteristic of entrained flow systems and the basis for the value of 450 lbs/hr ft^2 is the work of Boley and Landers (1969). Due to the nature of the entrained system modeling may be readily accomplished, and thus scaling up will be straightforward. Moderate temperatures of 450°C to 650°C only will be required to maximize the oil yield (based on the results presented in references 7 and 8). This temperature level is such that materials requirements are not stringent. Because of the relative geometric simplicity of the system (the pyrolysis reactor will be a straight tube or pipe) and the nature of operation, both maintenance and operating costs will be low. Pollution control requirements will be minimal. The system effluents will consist of the products, char and pyrolysis oil, dryer flue gases (water vapor, carbon dioxide, nitrogen, and oxygen) and ash (which will be sold as an agricultural additive or landfilled).

TABLE 1. ADVANTAGES OF ENTRAINED PYROLYSIS SYSTEM

High Throughput	450 lb Wood/hr/sq ft
Scaling up	Straight Forward
Moderate Temperatures	450°C - 650°C
Environmental Factors	Very Good

RESEARCH PROGRAM

The objectives of the research effort were to construct an entrained pyrolysis process research unit (PRU)

and to conduct an experimental program to obtain basic engineering data for maximum oil productions. The design and construction of the PRU have been completed and the details have been reported (Knight, J.A. et al, 1983).

FLOW DIAGRAM

A flow diagram of the PRU is given in Figure 1, and its operation is described in the following. Propane gas 1 and air 2 supplied by an air compressor are burned stoichiometrically in an inert gas generator, and the combustion products are cooled with a water spray 3 so that the gases leave saturated with water vapor. The exit stream from the inert gas generator is split into two streams. One of these 4 provides moderating gas for the burner and the other 5 provides conveying gas for the feed particles 6 . Propane 7 also fuels the burner which also operates stoichiometrically with air 8 supplied by a blower.

The mixture consisting of moderating gas, conveying gas, burner combustion products, and wood particles moves vertically upwards through the reactor tube in which the entrained pyrolysis takes place; the resulting mixture 9 consists of noncondensable gases, water vapor (entering moisture plus combustion and pyrolysis products), noncondensable gases, and pyrolysis oil vapors. In the cyclone, almost all of the char particles 10 are removed, and the stream 11 leaving the cyclone consists of noncondensable gases, water vapor, pyrolysis oil vapor, and some char fines. This mixture enters the condenser, and the pyrolysis vapors (and some water vapor) are condensed in the air-cooled condenser. The condensed phases 12 are removed via sumps and collection receivers, and the exiting mixture 13 consisting of noncondensable gases, water vapor, light oil vapors, an aerosol of oil, and possibly some fines enter the demister. In the demister most of the aerosol and fines are removed 14 . The resulting mixture 15 consisting mainly of noncondensable gases, water vapor, with some aerosol and fines enters the flare air is introduced, the mixture is burned, and the innocuous products of combustion 16 are exhausted to the atmosphere.

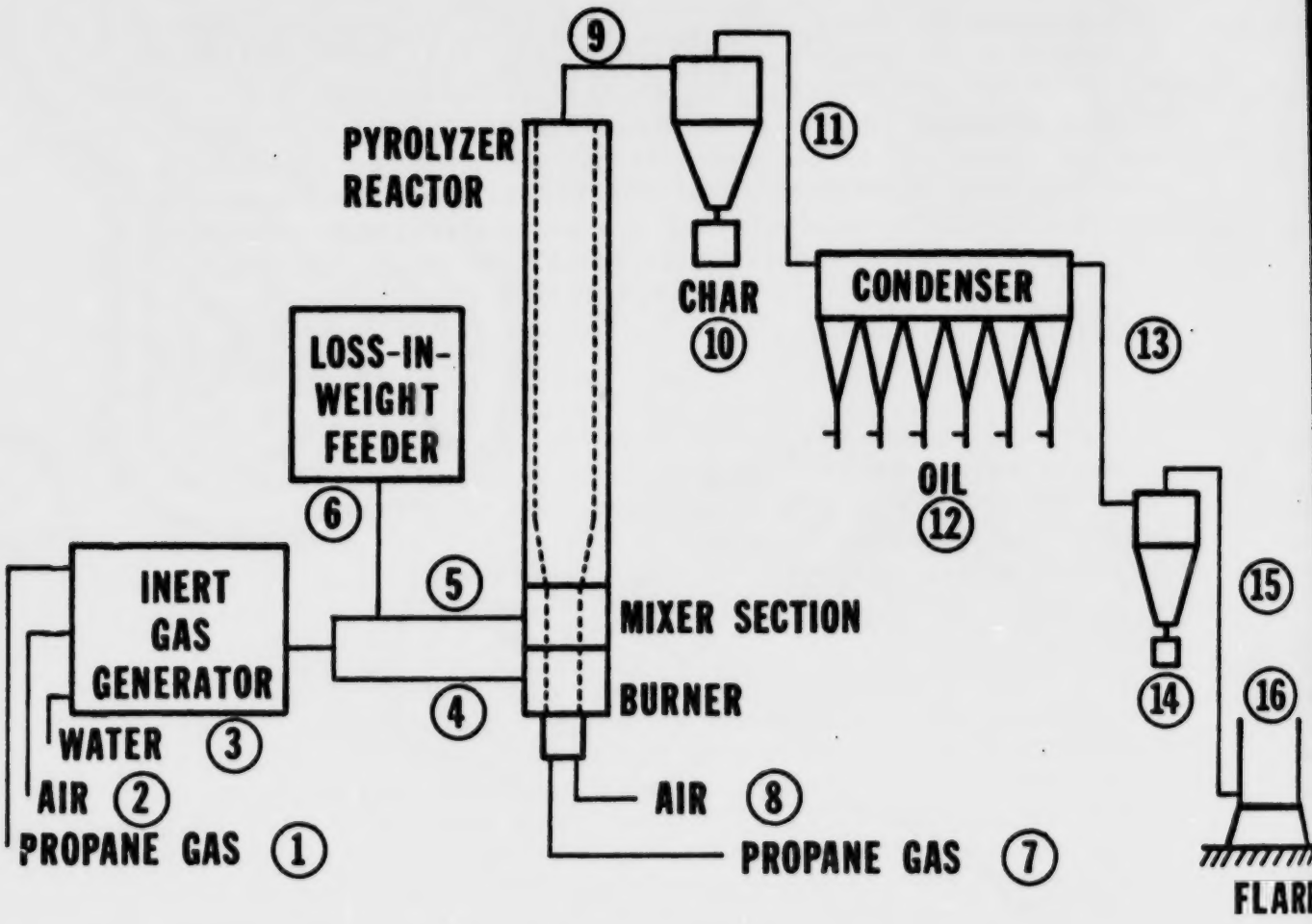

FIGURE 1. Entrained Flow Pyrolysis Process Research Unit

INSTRUMENTATION AND CONTROL

The PRU is instrumented so that appropriate temperatures, pressures and pressure drops can be obtained. All temperatures are measured with thermo-couples and the results recorded on strip-chart recorders. Pressures and pressure drops are determined with manometers, gauges and transducers. The results from the pressure transducers are also recorded on strip-chart recorders.

All input and output gaseous stream flow rates of the unit are determined with orifices. The amounts of solid and liquid products are determined by weighing. The input feed rate is determined with a loss-in-weight feeder, which automatically controls the feed rate at a specified rate. Stoichiometric conditions are maintained in the burner by a proportional control system. The burner may also be controlled to a specified gas temperature and has a flame detector with automatic shut off which is activated if the flame is extinquished.

DATA REDUCTION AND ANALYSIS

Both material and energy balances will be conducted for selected experimental runs. The energy balances will be based on measured heating values for the solid and liquid products. The heating values for the burner fuel and the gaseous products will be calculated from measured compositions obtained from GC analyses. Energy losses will include heat transferred from the unit and heat added to the cooling air in the condenser.

PRELIMINARY RUNS

A series of preliminary runs without feed have been conducted. The system operated well and no problems developed during the course of these runs. Several check-out runs have also been made using mixed hardwoods (red oak and white oak) as the feed stream. Although none of these runs have been completely satisfactory, they have provided valuable information concerning the operating conditions for the system. One of these runs will be discussed briefly in the following paragraph with typical conditions indicated.

For the run to be discussed, the feed rate was approximately 100 pounds per hour. The conditions were such that the gauge pressure at the pyrolyzer reactor inlet was 22 inches of water. At this location the temperature was about 900°F. At the reactor exit (the reactor is a vertically mounted eight inch 304 stainless steel pipe which is twenty one feet long) the temperature was about 850°F. After leaving the reactor, the mixture of gases, vapors, and solids enter the char cyclone. After leaving the cyclone, the gases and vapors pass through connecting piping and enter the condenser. There is a drop in temperature so that the gases enter the condenser at about 800°F. Part of the condensed water and oil is collected in six sumps. The remaining condensed phase remains as an aerosol most of which is collected in the demister. The mixture leaving the condenser is at a temperature of about 150°F. The mixture of gases, vapors and aerosol passes to the demister (a small cyclone) in which most of the aerosol is removed. The mixture subsequently passes to the flare where combustion of the noncondensable gases take place.

Typical feed and char analyses are presented in Table 2. The heating value for the char is typical of high carbon chars. Typical oil analyses for oils collected in various sumps is given in Table 3. These heating values are typical of oxygenated pyrolysis oils. The results of a noncondensable gas analysis is given in Table 4. The heating value given was calculated from the measured composition.

Table 5 presents a summary of conversion and heating value results for one of the preliminary runs. Based on the data presented in the table, the conversion of the wood feed (oak) to oil and light organics is 36.9 weight percent (based on moisture and ash free feed). As indicated, the higher heating value ratio is 94 percent.

Table 2. Feed and Char Analyses

	% Water*	% Volatiles	% Ash	Higher Heating Value Moisture and Ash Free (Btu/lb)
Feed	5.8	NA	.5	8,305
Char	1.2	27.1	4.7	13,165

*All values are weight %.

Table 3. Oil Analyses

Source	% Water	Higher Heating Value Moisture Free (Btu/lb)
First Sump	61.5	8,740
Fourth Sump*	6.3	10,025
Fifth Sump	10.4	8,930
Sixth Sump	24.0	8,690
Demister	18.1	9,970
Weighted Average	18.3	9,613

*Oil was not obtained in sumps two and three.

DISCUSSION

A number of test runs have been conducted with the PRU using a mixed hardwood feed. Oil yields of 36 to 40 percent with char yields in the range of 10 to 14 percent have been obtained. The results presented here gave a yield of oil and light organics of 36.9%. Oil yields higher than 40% are anticipated. A series of runs will be conducted in the near future to obtain operating conditions which maximize oil yields.

Table 4. Noncondensable Gas Analysis

Constituent	Mole %	Mass %
Ar	.9	1.2
O_2	.3	.4
N_2	70.6	68.6
CO	11.0	10.7
CO_2	11.4	17.4
H_2	3.8	.3
CH_4	1.3	.7
C_2H_4	.5	.5
C_2H_6	.1	.1
C_3H_6	.1	.1

Molecular Weight - 28.8

Higher Heating Value - 72.8 Btu/SCF (970 Btu/lb)

Table 5. Summary of Typical Conversion and Heating Value Results

Basis - 100 lbs Feed (ash and moisture free)

	Mass (lbs)	Higher Heating Value (Btu/lb)
IN		
Feed	100	8,305
OUT		
Char (ash and moisture free)	9.9	13,165
Oil (moisture free)	31.3	9,613
Condenser deposits (moisture free)	6.1	12,411
Noncondensable Gases	224.0	970
Aerosol and Light Organics	5.6	10,750*

$$\frac{\text{Higher Heating Value Out}}{\text{Higher Heating Value In}} \times 100 = 94^{**}\%$$

*Weighted average based on the measured heating value of the demister oil and on estimated value of 18,000 Btu/lb for the light organic.

**This does not include some minor combustibles in the inlet inert gas stream and burner combustion products.

ACKNOWLEDGMENT

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DESIGN ET CONSTRUCTION D'UN REACTEUR DE PYROLYSE SOUS VIDE FONCTIONNANT EN MODE SEMI-CONTINU ET BASÉ SUR LE CONCEPT DU FOUR À SOLES MULTIPLES.

par

Christian Roy, André Lalancette, Bruno de Caumia, Daniel Blanchette et Benoit Côté

Université de Sherbrooke
Département de génie chimique
Sherbrooke, (Québec) J1K 2R1

ABSTRACT

It has been shown that in the vacuum pyrolysis of wood chips, the gas and vapor products can be withdrawn either by the bottom or by the top of the reactor. The main features of the multiple hearth reactor used to conduct in a semi-continuous mode the thermal decomposition of wood are described. The Process Development Unit has been designed to treat 2 kg hr^{-1} of wood chips. Finally, the advantage of using the on-column capillary gas chromatograph for the analysis of wood-derived oils is discussed.

ESSAIS DANS UN REACTEUR BATCH AVEC SOUTIRAGE DES VAPEURS PAR LE HAUT

Nous avions décrit précédemment (1, 2) le rôle des principaux paramètres qui affectent directement les réactions pyrolytiques. En pyrolyse sous vide, les paramètres d'importance sont, outre la nature du substrat lui-même, le taux de chauffage de la matière traitée, la granulométric et surtout, la température de décomposition thermique, le temps de résidence dans l'enceinte du réacteur des vapeurs produites et la pression totale du système réactionnel.

Ces études fondamentales avaient été conduites au moyen d'une cornue métallique en position verticale où les vapeurs, les liquides et les gaz produits étaient soutirés par le bas du réacteur. La configuration du montage en question est présentée à nouveau à la Figure 1 ci-dessous.

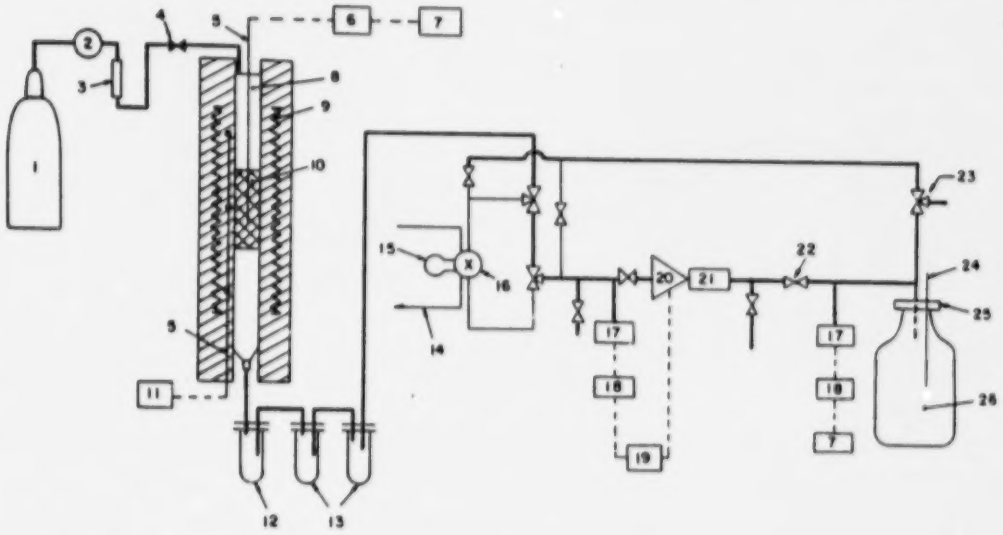

FIGURE 1: Schematic of batch vacuum pyrolysis set-up with withdrawal of vapors by the bottom.

Legend:

1. Nitrogen cylinder
2. Pressure gauge
3. Rotameter
4. Micrometric valve
5. Thermocouple
6. Thermocouple meter
7. Recorder
8. Retort
9. Three zone electric furnace
10. Sample
11. Temperature programmer
12. Cooling trap (ice and water)
13. Cooling traps (dry ice and acetone)
14. Carrier gas to chromatograph
15. Sampling loop
16. Gas sampling valve
17. Electronic manometer head
18. Digital readout
19. Pressure controller
20. Automatic vacuum exhaus
21. Vacuum pump
22. Two-way manual valve
23. Three-way manual valve
24. Thermometer
25. Vacuum seal
26. Gas collecting bottle

Dans ce système, la disposition du lit de biomasse ne permettait pas toutefois d'évaluer si les produits liquides

récupérés après refroidissement dans les trappes de condensation à la suite du réacteur provenaient d'une réaction de "liquéfaction" du combustible solide initial, ou si ces produits résultaient plutôt de réactions de "sublimation" directe de la matière en produits gazeux condensables. L'hypothèse qu'il nous fallait à présent tester en vue de la construction et de l'opération d'un réacteur de pyrolyse sous vide ayant un possible intérêt commercial était de vérifier s'il était possible de soutirer au-dessus du lit de biomasse les vapeurs ou liquides produits. Dans l'affirmative il y aurait un grand intérêt d'opérer un réacteur commercial fonctionnant selon ce principe puisqu'il serait alors possible de séparer immédiatement les produits liquides organiques désirables des solides résiduels. Les réactions pyrolytiques à pression réduite consistent soit en une "liquéfaction" de la matière solide initiale suivie d'une vaporisation de ces liquides, facilitée par ailleurs par les faibles pressions en jeu dans le système, soit en une "sublimation" directe de la matière en vapeurs subséquemment condensables, soit finalement en une combinaison de ces deux phénomènes.

L'arrangement utilisé pour tester la possibilité de soutirer au-dessus du lit de biomasse des produits organiques liquides est décrit à la Figure 2 de l'article. En parallèle, le montage de laboratoire ainsi construit permettait de tester à une échelle réduite le comportement des différentes composantes d'une sole représentative du réacteur entier (UDP) afin de réaliser la mise au point définitive à partir de ce modèle. Aussi ce réacteur de laboratoire allait servir à produire des huiles pyrolytiques en quantité suffisante pour effectuer des essais de raffinage ou d'analyse.

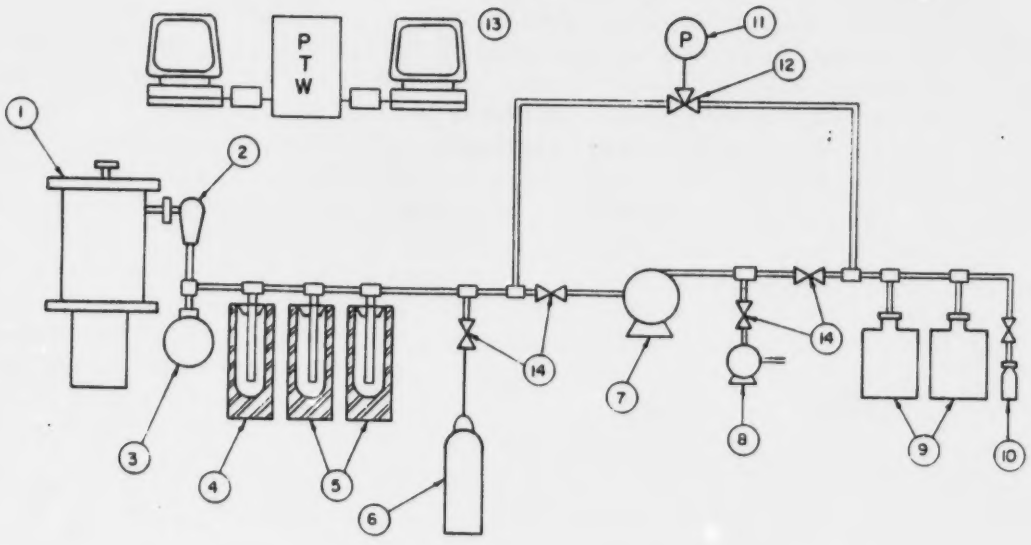

FIGURE 2: Schematic of batch vacuum pyrolysis set-up with withdrawal of vapors by the top.

Legend:

1. Reactor
2. Condenser
3. Receiver
4. Cooling trap (ice and water)
5. Cooling traps (dry ice and acetone)
6. Inert gas
7. Vacuum pump
8. Auxiliary vacuum pump
9. Gas collecting bottles
10. Sampling bottle
11. Electronic manometer head
12. Solenoid valve
13. Microprocessor
14. Two-way manual valves

Un dessin de détails du prototype est présenté à la Figure 3 du texte. L'enceinte du réacteur est un cylindre d'acier d'une hauteur de 30 cm, d'un diamètre intérieur de 25 cm et d'une épaisseur de 0,64 cm. Le volume utile du réacteur est de 10 litres. Un tube de 2,5 cm de diamètre est soudé au centre du couvercle et un autre est rattaché à la partie latérale supérieure du réacteur. Sur ces tubes sont soudés des brides de 6,5 cm de diamètre. Dans le premier cas cette sortie permet l'introduction d'un thermocouple à l'intérieur de l'enceinte alors que dans le deuxième cas la sortie permet l'évacuation des gaz produits lors de la pyrolyse. Un passe-fils est soudé sur la partie latérale inférieure de l'enceinte pour permettre l'alimentation électrique et la lecture de thermocouples placés à l'intérieur.

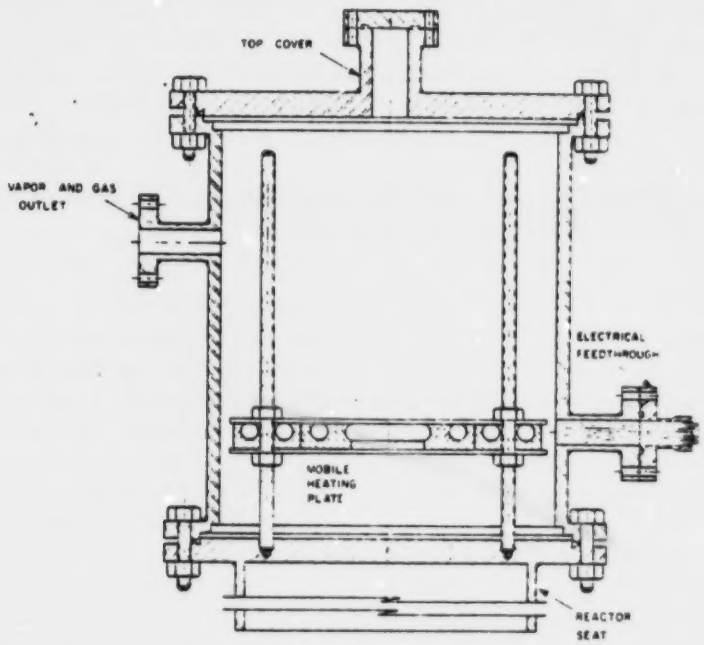

FIGURE 3: Draft of 10ℓ batch vacuum pyrolysis reactor.

Le lit de biomasse à traiter repose sur un plateau chauffant, lequel peut être ajusté et maintenu à la hauteur désirée dans le réacteur. Cet arrangement permet de tester l'effet d'espace d'évacuation libre au-dessus du lit de matières en réaction.

Les vapeurs et gaz produits au cours des réactions pyrolytiques sous vide sont évacués par le haut du réacteur puis refroidis dans un train de condenseurs en pyrex (voir Figure 2). L'agent refroidissant est de l'eau tiède en circulation en première étape, de l'eau glacée en second lieu et un mélange de glace sèche/acétone à -80°C par la suite. Les gaz incondensables sont acheminés vers une bouteille en pyrex mise initialement sous vide; les gaz y sont accumulés pour fin d'analyse chromatographique ultérieure. Une pompe à vide de 75ℓ min^{-1} assure le maintien du vide au niveau désiré dans l'enceinte réactionnelle. (<5 torrs au point de lecture indiqué à la Figure 2).

Le contrôle de la température est un facteur primordial en pyrolyse. Le système a donc été entièrement automatisé pour cette fin. Le contrôle s'effectue avec un microordinateur qui établit à l'aide d'une cédule préprogrammée l'évaluation de la température requise. De plus, pour éviter les gradients de températures trop élevés à l'intérieur du lit de biomasse, l'ordinateur compare la température prise à la surface du plateau chauffant avec celle prise dans le milieu du lit. Si l'écart dépasse 100°C l'ordinateur arrête la programmation et attend que l'écart se rétablisse à la normale pour continuer. La lecture des températures s'effectue toutes les 20 secondes. Le microordinateur de base choisi pour effectuer cette opération est le Super Pet de Commodore, tel que modifié par Control Micro-Systems, Inc. (Montréal).

Le système ne possédant qu'une jauge de pression alors que 2 pressions différentes sont d'intérêt (soit la pression dynamique du système et la pression des gaz accumulés dans les bouteilles), une valve solénoïde à trois voies contrôlée par microordinateur permet la lecture désirée. L'acquisition des données de température et de pression est effectuée automatiquement par l'ordinateur; ces données sont transférées sur disque régulierement. Dans le même temps les données sont imprimées graphiquement ce qui permet de suivre visuellement la progression de la réaction.

Les manipulations expérimentales avec ce pyrolyseur de 10 litres s'effectuent selon la séquence suivante: montage, test d'étanchéité au vide, chauffage et réaction, refroidissement du réacteur, démontage et enfin analyse des produits.

À l'étape du montage on place dans l'enceinte et sur le plateau chauffant la matière à pyrolyser laquelle a été préalablement pesée (typiquement, 1 kg d'échantillon). On ferme alors hermétiquement le réacteur après avoir disposé le thermocouple de contrôle dans sa gaine à travers le couvercle du réacteur. Le train de condenseurs est ensuite installé après avoir fait les pesées nécessaires et des mélanges eau/glace et acétone/glace sèche sont préparés afin d'obtenir le refroidissement requis. Tout le système est alors mis sous vide à l'aide de la pompe mécanique. On s'assure initialement de l'étanchéité au vide du système en limitant l'afflux d'air extérieur dans l'enceinte à 10^{-1} torr min^{-1}.

Le contrôle du chauffage du plateau du réacteur s'effectue jusqu'à ce que la température finale désirée soit atteinte. On ne note qu'un très faible gradient de température sur le plateau même.

La réaction est complète lorsque la pression des gaz accumulés dans les bouteilles se stabilise. Il y a alors arrêt du chauffage électrique. On introduit après une période de refroidissement du réacteur de l'argon jusqu'à la pression atmosphérique dans le but de réduire autant que possible le contact des produits liquides et solides avec l'oxygène ambiant suite à l'ouverture du réacteur. On détermine alors le poids des produits liquides et solides obtenus alors que le poids des gaz incondensables est calculé indirectement suite à une analyse chromatographique. Quelques résultats d'analyse des produits liquides et gazeux obtenus suite à la pyrolyse sous vide du peuplier faux-tremble seront présentés un peu plus loin dans l'article. Ce montage permet d'obtenir des bilans de matière de l'ordre de 99%.

On a effectué la pyrolyse sous vide de copeaux de bois de tremble Populus Tremuloïdes semblables à ceux utilisés au cours d'une expérience précédente avec le réacteur de pyrolyse batch de 1ℓ muni d'une évacuation des

vapeurs par le bas (voir Figure 1). Les résultats sont présentés sur une base comparative au Tableau 1 ci-dessous.

Tableau 1 - Rendements comparés des produits pyrolytiques obtenus à partir du bois dans un réacteur de pyrolyse sous vide avec soutirage des vapeurs par le bas et par le haut du réacteur.

	Batch 1ℓ Soutirage par le bas	Batch 10ℓ Soutirage par le haut
Température finale (°C)	417	419
Taux de chauffage (°C min $^{-1}$)	2	1,5
Pression maximale enregistrée (mm Hg)	2	2
Granulométrie, copeaux sans écorce (mm/mm)	4,76/19,0	4,76/19,0
Rendements sur une base organique (% en poids):		
Huiles pyrolytiques	52,4	47,5
Eaux pyrolytiques	14,2	17,0
Char	21,5	22,4
Gaz	11,9	13,1

Les rendements en huiles pyrolytiques obtenus avec le réacteur muni d'une évacuation par le haut sont inférieurs à ceux obtenus par l'autre configuration. La différence notée serait attribuable à notre avis à des réactions de repolymérisation des macromolécules sur les particules solides en voie de carbonisation. Le désavantage ne nous apparaît pas significatif toutefois en regard de l'avantage obtenu par la séparation immédiate des huiles et des solides résiduels. Un rendement intermédiaire en huiles est par ailleurs prévisible lors de l'opération de l'UDP puisque dans ce cas le lit de biomasse sera moins dense.

UNITÉ DE DÉVELOPPEMENT DE PROCÉDÉ

Les objectifs principaux visés par l'opération de l'UDP sont de confirmer les rendements et les bilans de masse obtenus à l'aide des prototypes batchs de pyrolyse sous vide, d'évaluer les conditions optimales d'opération du système, d'estimer l'efficacité thermique globale de l'ensemble réactionnel, de déterminer les données économiques préliminaires du procédé et enfin de proposer une configuration finale pour l'ensemble du système en vue d'une application commerciale.

Un diagramme d'écoulement de l'UDP présentement construite et en voie d'être testée est présenté à la Figure 4 de l'article. L'unité comprend un bac de 50ℓ contenant les copeaux de bois et reposant sur un transducteur de poids relié au microordinateur. Ce récipient est étanche au vide; il comprend un dispositif permettant l'alimentation dans un mode en semi-continu, typiquement de l'ordre de 1 à 2 kg hre^{-1}, des copeaux de bois dans le réacteur de pyrolyse sur lequel il repose. En fait l'alimentation à bas régime est ici réalisée par le biais d'un moteur pas-à-pas lequel permet le déversement du bois par impulsions reproduites à fréquence régulière.

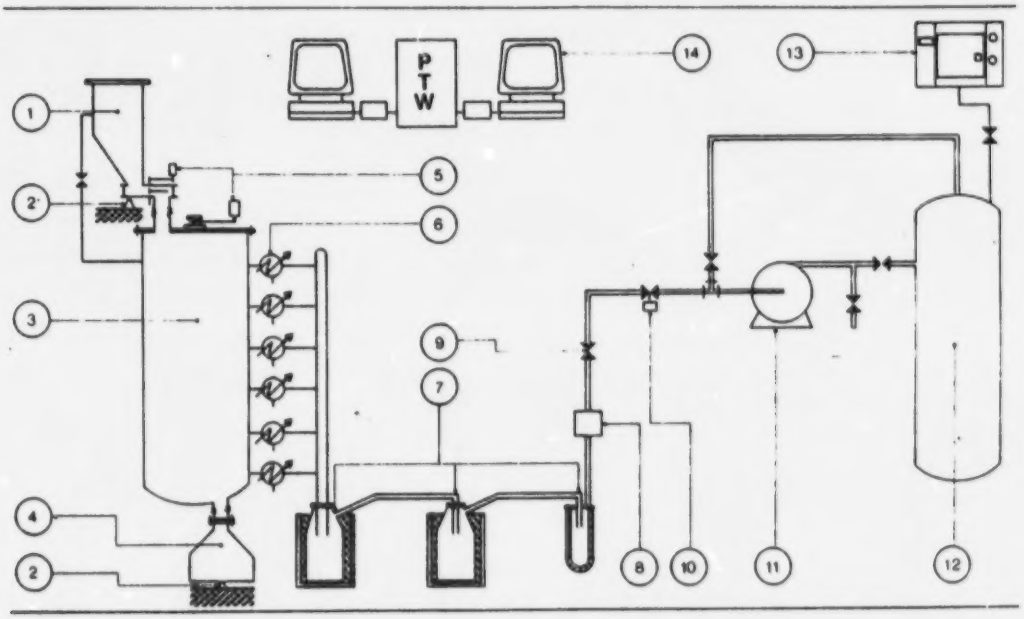

FIGURE 4: Flow diagram of vacuum pyrolysis Process Development Unit

Legend:

1. Hopper with vacuum seal
2. Weight transducer
3. Multiple hearth reactor
4. Char receiver
5. Stepping motors
6. Cooler
7. Liquid receivers
8. Active carbon trap
9. Ball valve
10. Automatic valve
11. Mechanical vacuum pump
12. Noncondensable gas tank
13. Gas chromatograph
14. Control and data acquisition system

Le réacteur vertical de pyrolyse sous vide est basé sur le concept du four à soles multiples. La dimension du réacteur est de 2 m de hauteur par 0,7 m de diamètre. Il comprend 6 soles ou plateaux, chauffés électriquement. Chacun des plateaux est contrôlé et chauffé indépendamment l'un de l'autre; le contrôle est assuré par microordinateur de façon qu'un plateau entier soit réglé à une seule et même température. L'alimentation électrique et le passage des thermocouples sont assurés par des passe-fils qui sont fixés sur le couvercle et permettent de garder l'étanchéitté au vide du système. Les copeaux de bois sont déversés mécaniquement à l'aide de bras et de grattoirs depuis le premier plateau jusqu'au bas du réacteur. L'agitation est effectuée à l'aide d'un second moteur pas-à-pas lequel est également contrôlé par microordinateur.

Au niveau supérieur de chaque plateau chauffant se trouve une sortie permettant l'évacuation des vapeurs et gaz produits. L'évacuation est réalisée par une pompe à vide d'une capacité de 1200ℓ min^{-1}. Les vapeurs condensables sont récupérées et distribuées dans un train de condenseurs tel que représentés dans la Figure.

Les résidus solides sont récupérés dans un bac de 50ℓ reposant sur un transducteur de poids relié au microordinateur. Les gaz incondensables sont récupérés dans un réservoir métallique de 450ℓ lequel a été préalablement mis sous vide. Les gaz qui s'accumuleront dans ce réservoir seront agités afin de prévenir toute ségrégation des composants de différents poids moléculaire. Un échantillonnage et une analyse automatiques des gaz seront effectués à partir de ce réservoir.

Plusieurs instruments de mesure et de contrôle sont installés sur les différentes unités du montage. La mesure de l'alimentation en bois est assurée par un transducteur de poids qui donne la valeur en continu du poids de bois dans le réservoir d'alimentation; la dérivée de la courbe ainsi obtenue correspond au débit de bois déversé. Le signal sortant du transducteur est alors envoyé au microordinateur lequel commande le moteur pas-à-pas pour la régulation de la vitesse de rotation adéquate du mécanisme de déversement du bois à la sortie de l'alimenteur. Tel que mentionné précédemment, un second moteur pas-à-pas assure la rotation des grattoirs dans le réacteur principal. Un transducteur de poids est installé sous le bac recevant le char pour mesurer le taux d'accumulation des solides résiduels.

Chaque plateau est maintenu à une température spécifique. Deux thermocouples sont installés dans chaque plateau: un pour effectuer le contrôle de la réaction proprement dite et un second afin de s'assurer qu'en tout temps la température atteinte du plateau chauffant sera telle qu'il n'existe pas de possibilité de brûler les éléments. Il existe aussi un thermocouple près de chacune des sorties de gaz et vapeurs du réacteur et quelques thermocouples sont installés sur les parois du réacteur puisqu'on chauffe le corps du réacteur afin d'empêcher la recondensation des gaz produits. Dans ces cas également le microordinateur permet le contrôle des températures en relayant les signaux adéquats aux éléments chauffants.

Pour fin de sécurité, un détecteur d'oxygène a été installé pour détecter toute entrée d'air dans la zone réactionnelle. En tel cas il y aurait arrêt immédiat de l'opération et envoi d'un gaz inerte pour empêcher tout danger d'explosion.

Le contrôle du débit fourni par la pompe à vide est assuré par une valve automatique laquelle est également actionnée via le microordinateur. Le microordinateur accepte également des signaux envoyés par les lecteurs de pression installés dans le réacteur et le réservoir d'accumulation des gaz non condensables.

PROCÉDURES ANALYTIQUES

Analyse automatisée des gaz non condensables

Les gaz non condensable (e.g., H_2, CO, CO_2, CH_4, C_nH_m) obtenus à différentes températures pyrolytiques sont analysés par chromatographie gazeuse. Cependant une cédule d'analyse complète requiert environ 50 minutes par échantillon. Il existe donc un intérêt évident à automatiser le système d'échantillonnage et d'analyse des gaz afin d'accroître le nombre d'analyses pouvant être effectuées à intervalles de températures rapprochées.

Nous avons réalisé dans nos laboratoires un tel montage d'échantillonnage automatique; un schéma-bloc en est présenté à la Figure 5. La boîte d'échantillonnage des gaz, laquelle comprend 16 boucles d'échantillonnage, peut-être transportée et raccordée sur n'importe quelle unité réactionnelle produisant des gaz. L'échantillonnage se fait de façon automatique. On raccorde par la suite au moyen de 2 connections simples la boîte d'échantillonnage contenant les boucles d'échantillonnage au chromatographe pour compléter l'analyse automatisée. Cette unité d'échantillonnage et d'analyse est opérationnelle dans nos laboratoires.

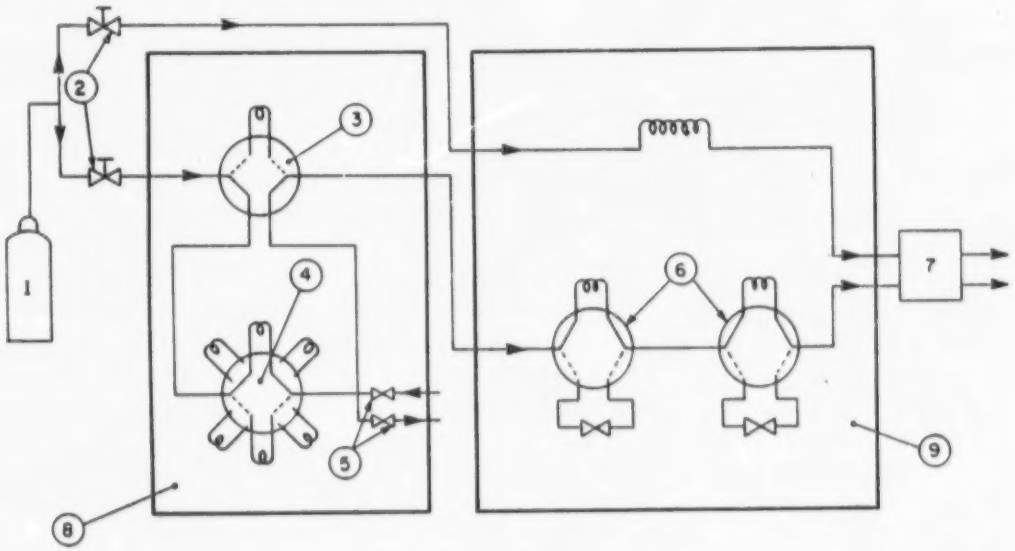

FIGURE 5: Automatic gas analysis and sampling device.

Legend:

1. Carrier gas
2. Regulating valves
3. Injection valve
4. Sampling valve
5. Solenoid valves
6. Four-way valves
7. Thermal conductivity detector
8. Sampling box
9. Gas chromatograph oven

Analyse du pyroligneux

L'analyse des produits organiques présents dans le pyroligneux était jusqu'ici en partie effectuée dans nos laboratoires à l'aide de chromatographes gazeux sur colonne capillaire en mode d'injection split/splitless (Ménard, et al 1982). Un désavantage de cette technique est qu'une portion significative des vapeurs injectées dans l'appareillage est éjectée vers l'extérieur du chromatographe. Ceci a pour effet de créer une ségrégation entre les produits introduits dans la colonne chromatographique et ceux rejetés vers l'extérieur, ce phénomène étant attribuable à la différence de volatilité des divers composants. Cet effet est d'autant plus marqué qu'il existe un grand écart entre les températures d'ébullition des corps injectés pour analyse, ce qui est le cas pour le type d'huiles pyrolytiques obtenues par pyrolyse sous vide de la biomasse. On contourne généralement cette difficulté en établissant des facteurs de correction qui tiennent compte de la différence de volatilité des divers composants. Cette méthode est toutefois indirecte et donc sujette à des erreurs d'interprétation.

Il existe maintenant sur le marché un type de chromatographe gazeux permettant l'introduction complète de l'échantillon à analyser directement dans le support chromatographique. Il s'agit du chromatographe sur colonne capillaire avec mode d'injection "on-column". Tout l'échantillon liquide à analyser est directement introduit avec une seringue ultra-fine dans la colonne, réduisant par le fait même les possibilités de réaction de ségrégation ou de décomposition thermique des composants sensibles à la chaleur.

Nous avons effectué avec succès ce genre d'analyse pour un mélange synthétique de composés organiques que l'on retrouve généralement dans les huiles pyrolytiques dérivées du bois. La Figure 6 illustre le degré de résolution ainsi que la stabilité de la ligne de base obtenus avec cet appareillage.

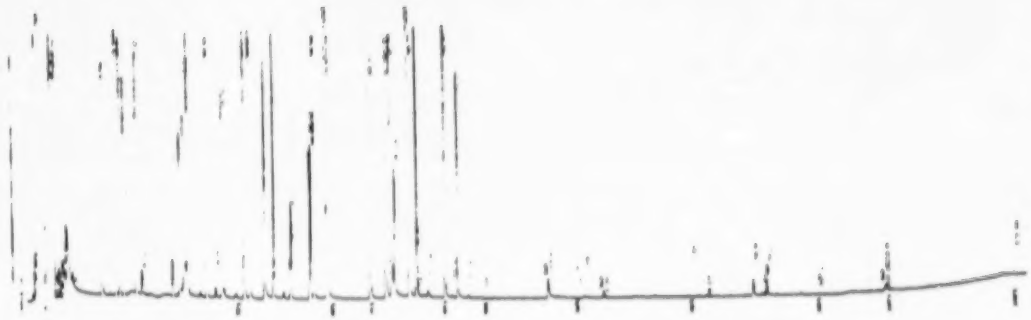

FIGURE 6: **On-column chromatogram of organic liquid synthetic mixture.**

Operating conditions:

Capillary gas chromatograp , Varian 3770
Durabond 1701, 31 m length, 0.32 mm I.D., 0.25 mm
F.I.D. detector, 300°C
>3 cc/min carrier gas
300 cc/min air; 30 cc/min H_2; 30 cc/min make-up

Injection: 40°C; 80°C/min up to 280°C; 99 min at 280°C
Column: 40°C during 3 min; 1°C/min up to 280°C
Volume: 1 mℓ

Par ailleurs, nous avions discuté dans une publication précédente la difficulté de la détermination de l'eau dans un mélange organique complexe. À notre avis la technique basée sur le réactif de Karl-Fischer offrait les meilleures garanties de précision en particulier pour la détermination de l'eau dans les pyroligneux dérivés de la biomasse. Cette observation est à présent appuyée de façon plus évidente encore à partir des résultats comparatifs indiqués au Tableau 2 de notre texte.

Tableau 2 - Contenu en eau (% en poids) des fractions distillées provenant de la distillation Dean-Stark de divers échantillons liquides dérivés de combustibles.

Combustible initial	% Eau (Karl-Fischer)
Houille grasse	99,2
Huiles lourdes de raffinerie	99,0
Bitumes (procédé CANMET)	97,8
Fraction TR7-B (plan pilote d'Albany	96,0
Tourbe	92,7
Peuplier faux-tremble (pyrolyse conventionnelle	83,1
Peuplier faux-tremble (pyrolyse sous vide)	62,1

L'analyse des résultats du Tableau 2 permet d'observer que l'application de la méthode de Dean-Stark est plus appropriée dans le cas des combustibles de rang élevé (ce qui correspond d'ailleurs au champ d'application de la méthode selon les standards) mais pas du tout dans le cas des combustibles de rang intermédiaire (e.g., tourbe) ou peu élevé (e.g., bois). Il est à noter que les composés organiques issus des réactions pyrolytiques sous vide du bois se retrouvent, par rapport à la situation de pyrolyse atmosphérique, en plus abondante quantité dans la phase acqueuse. Ceci pourrait s'expliquer par une polarité plus prononcée des composants issus des réactions à pression réduite. Une analyse, en cours, plus détaillée des distillats permettra de confirmer ou non cette hypothèse.

REMERCIEMENTS

La contribution technique de MM. Jean Fréchette, Michel Gagné, Marc Renaud et Sylvain Harbec a été grandement appréciée des auteurs.

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Section 5

CHARACTERIZATION OF LIQUEFACTION PRODUCTS

LIQUID FUEL PRODUCTION FROM SEWAGE SLUDGE

T.R. BRIDLE and H.W. CAMPBELL
Environment Canada
Environmental Protection Service
Wastewater Technolgy Centre

INTRODUCTION

Sewage sludge is an unavoidable by-product of watewater treatment and roughly one tonne of sludge is generated per 4,540 m^3 (1.0 million gallons) of wastewater treated (Black and Schmidtke, 1979). Disposal of sewage sludge is an expensive process and normally constitutes up to 50% of the total annual costs for wastewater treatment. It is estimated that over 500 000 tonnes of dry sewage sludge are produced annually in Canada and disposed of at a total cost of about $104 million (Bridle, 1982). Major sludge disposal options used in Canada include agricultural utilization, landfilling and incineration, with disposal costs ranging from about $126/tonne for agricultural utilization to over $300/tonne for incineration (Simcoe Engineering, 1980).

In addition to disposal costs, other considerations such as a projected doubling of sludge production in the next decade (Black and Schmidtke 1979) (Bunch, 1981), potential restrictions on agricultural utilization, and an ever increasing difficulty in licensing disposal sites, indicate the need for alternative resource recovery oriented solutions.

TECHNOLOGY REVIEW

Numerous sludge processing options have the potential to convert a fraction of the organic material in sewage sludge into usable energy, but only a few have been demonstrated to be viable net energy producers at full scale. Processes such as starved air incineration, gasification and liquefaction are in development stages and a more thorough review of these is presented elsewhere (Bridle et al 1983).

The most promising technology has been developed in Germany where researchers form Tubingen University have demonstrated a very simple process to convert sewage sludge to oil and char (Bayer and Kutubbudin, 1982). The process comprises heating dried sludge to 300-350°C in an oxygen free environment for about 30 minutes. Significant advantages of this process are that it operates at only slightly above atmospheric pressure and that no additives are required. The researchers postulated that vapour phase catalysed reactions convert the organics in sludge to straight chain hydrocarbons. The German researchers have demonstrated oil yields ranging from 18-27% and char yields from 50-60%. The oil has a heating value of approximately 39 MJ/kg and the char about 15 MJ/kg. Energy balance calculations indicate the process is a net producer of energy provided that the sludge is mechanically dewatered to about 20% solids. It has been estimated that a net energy production of 10-15 MJ/kg sludge could be demonstrated at full scale.

Environment Canada contracted with Dearborn Environmental Consultants to assess this technology in the Canadian context. A two-phase program was developed. The first phase comprised batch experimentation to validate the German process with Canadian sludges and to generate some limited process design information. The second phase involves construction of a lab scale continuous reactor system for the generation of process design information, which will allow development of cost data to assess the potential of the technology at full scale.

EXPERIMENTAL METHODS AND TECHNIQUES

Raw sludges containing a mixture of primary and waste activated sludge (WAS) from sewage treatment plants in Toronto, Hamilton and Burlington, Ontario were evaluated during this study. All sludges were oven dried (70°C) to about 90-95% solids. Analyses of these sludges indicates they were similar in composition with volatile solids of 60-64%, calorific values of 16-18 MJ/kg and carbon contents of 33-36% (Table 1).

Table 1. Sludge Analyses (dry Weight Basis)

Parameter	Sludge Toronto	Hamilton	Burlington
Volatile Solids (%)	60.3	60.5	63.6
Calorific Value (MJ/kg)	16.0	17.5	17.8
Carbon(%)	33.28	34.44	36.34
Hydrogen (%)	4.91	5.17	5.31
Nitrogen (%)	3.44	3.15	3.63
Sulphur (%)	0.78	0.96	0.68
Oxygen (%)	57.59	56.28	54.04
Nickel (µg/g)	63	222	12
Copper (µg/g)	863	655	668
Zinc (µg/g)	970	2416	1299
Chromium (µg/g)	1260	1260	129

The batch reactor, a pyrex tube 79 mm in diameter and 720 mm in length, was heated in a three-zone Lindberg furnace under a nitrogen atmosphere (Figure 1). Off-gases were condensed in a trapping system as shown, using ice as the coolant. Non-condensable gases (NCG) were vented from

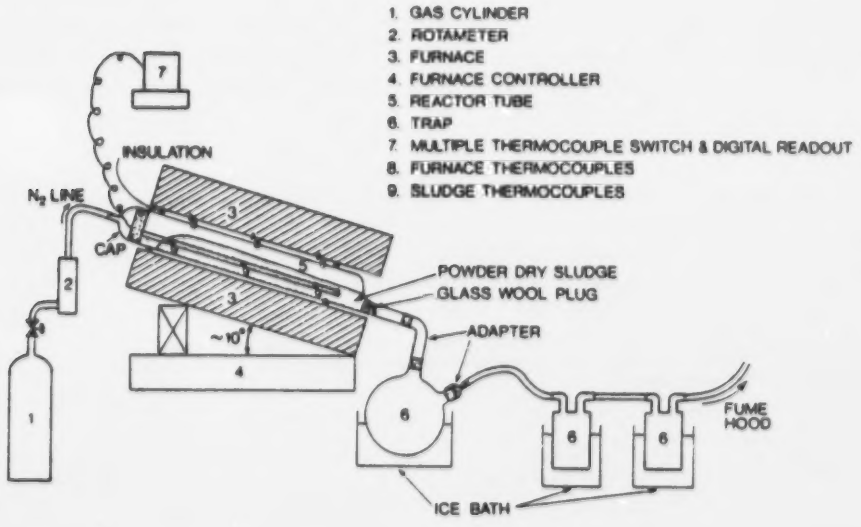

FIGURE 1. Batch Experimental Equipment

the system. A run was conducted by charging 550 g of dried sludge into the reactor and deaerating with nitrogen. Once operating temperature had been reached, the nitrogen purge rate was reduced. When all visible signs of reaction i.e., gas/oil flow ceased, the heat was switched off and the nitrogen purge rate was increased for approximately 30 minutes. the system was dismantled and the char, oil and pyrolytic water collected and stored for analysis. Oil/water separation was achieved using a separatory funnel.

RESULTS

The results will be discussed with respect to both process performance and environmental considerations.

Process Performance

Operating test conditions and results from the bulk of the experimental program are shown in Table 2. All the data is expressed on a dry sludge basis (corrected for the normal 4-7% moisture present in sludge) and the calorific

Table 2. Test Run conditions and Results

		OPERATING CONDITIONS		RESULTS							
				Oil			Char				
RUN NUMBER	SLUDGE	Temp. (°C)	Other Comments	Yield (%)	Cal.Value (mj/kg)	Viscosity (centistokes)	Yield (%)	Cal.Value (mj/kg)	Non-Condensable Yield (%)	Pyrolytic Water Yield (%)	Thermal Efficiency (%)
1,20	Hamilton	400	Optimal	20.8	36.40	Solid*	59.5	9.86	11.6	8.1	81.9
9-10	Burlington	450	Optimal	21.1	37.43	31.1	52.5	10.68	13.2	13.1	77.7
14,15,16	Toronto	450	Optimal	24.1	35.13	60.5	53.7	10.08	13.3	8.8	83.2
11,12,13	Toronto	350	Low temperature	12.8	33.32	Solid	65.6	12.00	10.3	11.2	79.3
22	Hamilton	450	High temperature	22.3	38.87	Solid	54.6	9.39	12.1	11.0	80.4
29	Hamilton	400	Centrifuge with polymer	20.6	37.29	Solid	60.4	8.27	11.7	7.3	87.5
30	Hamilton	400	Centrifuge without polymer	15.6	37.38	Solid	64.9	8.96	10.8	8.7	82.7
31	Hamilton	400	Second reactor, empty	19.0	37.49	Solid	60.0	11.07	12.0	9.0	80.1
32	Hamilton	400	Second reactor, char	17.2	38.18	39.5	59.9	11.07	13.0	9.9	77.0
33	Hamilton	400	Second reactor, catalyst	19.0	37.49	31.0	56.8	10.01	14.8	9.4	75.0

*Solid defined as >214 centistokes

values are expressed on a total solids basis (not corrected for volatiles). The non-condensable gas (NCG) yield was

calculated by difference. Analysis of the NCG, by GC, indicated that it contained roughly 6% methane, 10% carbon monoxide with the remainder comprising mostly carbon dioxide and nitrogen. The calculated calorific value is approximately 2.0 MJ/kg of NCG.

Optimal test conditions were defined as:

- optimal conversion temperature as determined by differential scanning calorimetry,
- ramping (linear increase with time) to operating temperature at 10°C/minute, and
- continuous nitrogen purge at 7 mL/s.

(i) Different Sludges: Sludges from Hamilton, Burlington and Toronto were tested. The average results achieved for these sludges under optimal conditions are shown at the top of Table 2. As can be seen, each of these sludges are amenable to conversion, with oil yields ranging from 20.8 to 24.1% and thermal efficiencies ranging from 77.7 to 83.2%. Throughout this test, thermal efficiency is defined as the energy recovered in the oil, char and NCG as a percentage of that available in the sludge. The average calorific value of the oil generated varied from 33.13 to 37.43 MJ/kg and for the char, from 9.86 to 10.68 MJ/kg. The viscosity of the oils generated appeared to be sludge specific. These variations in performance most likely reflect the variations in sludge quality from site to site. Within the constraints of the experimental program (i.e., batch conditions) the reproducibility within sludge batches was considered acceptable, i.e., generally less than 10% variation in oil yield.

(ii) Effect of Operating Temperature: Operating temperature has a pronounced effect on oil yield. As mentioned, optimal operating temperature was defined using differential scanning calorimetry (DSC). A DSC output for

Toronto sludge (Figure 2) indicates two exotherms, one at 300°C and one at 400°C. These exotherms have been attributed to lipid and protein decomposition and subsequent catalysed conversion to hydrocarbons. Oil yield is proportional to the area under these exotherms. It can clearly be seen that a significant reduction in oil yield would be expected by operating at 350°C rather than the optimal of 400-450°C. This was confirmed experimentally using Toronto sludge, (Runs 11, 12, 13 compared to Runs 14, 15, 16) which showed a reduced oil yield from 24.1 to 12.8% with a concomitant decrease in thermal efficiency. However, operating at temperatures above optimal did not appear to significantly affect oil yield or thermal efficiency (Hamilton sludge, Run 22 compared to Runs 1, 20).

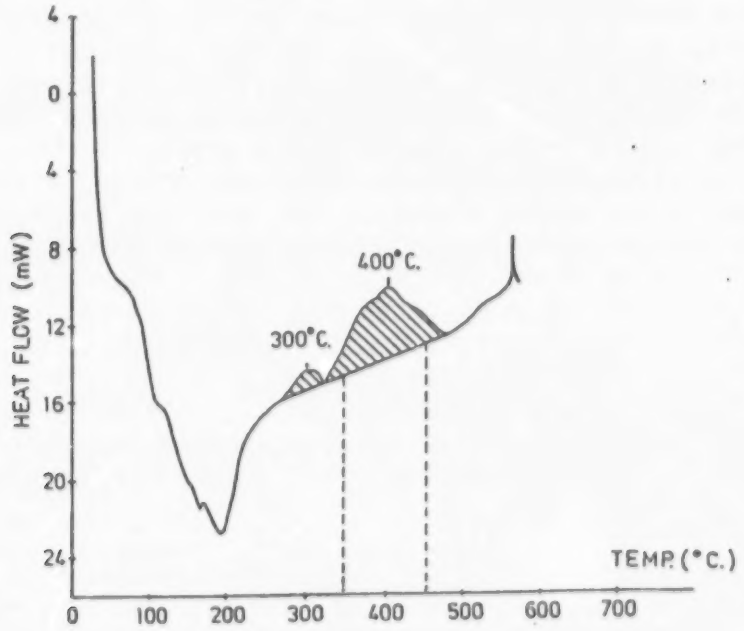

FIGURE 2. DSC Output for Toronto Sludge

(iii) Effect of Sludge Dewatering: -- The process must operate with dry sludge and from an economic viewpoint, mechanical dewatering (to remove as much water as possible) will be mandatory prior to thermal drying. To assess the impact that sludge dewatering may have on the process, batches of Hamilton sludge were dewatered with and without polymer addition (Runs 29, 30). Solids capture varied from 100% (oven drying, Runs 1, 20) to 96.4% (centrifugation with polymer addition, Run 29) and to 72.5% (centrifugation without polymer addition, Run 30). the data indicate a

profound effect on oil yield. With poor solids capture the oil yield decreased for roughly 21% to 15.6%. This is to be expected since oil is produced from the biomass, which at poor solids capture would be preferentially lost in the centrate. Thus, at full scale, performance of the dewatering step can have a significant impact on the total oil yield, and thus the overall economics of the entire process.

(iv) Effect of Extended Gas and Gas/Solid Contact Time: A dual reactor system was set up to evaluate whether extended gas and gas/solid contact time had an effect on product yield and quality. The second reactor, identical to the original one, was placed in a vertical position downstream of the first reactor. Vapours from the first reactor were passed through this second reactor prior to condensation. The temperature in the second reactor was maintained at the optimal level.

Three runs were conducted in this mode. The first used an empty reactor (Run 31) to assess the effect of increased gas residence time. The second and third runs (Runs 32, 33) were conducted with the second reactor packed with either char or a decarboxylation catalyst (copper).

These two runs were conducted to establish whether increased gas/catalyst contact time had any effects. The data in Table 2 indicate that increased gas/catalyst contact time had a dramatic effect on oil quality. It can be seen that oil viscosity was significantly reduced when extended gas/catalyst contact time was permitted. Under normal conditions the oil is solid at room temperature i.e, viscosity is > 200 centistokes. This was reduced to 39 centistokes when char was used as the catalyst and 31 centistokes when a copper catalyst was used. The reduced thermal efficiencies for these runs was probably due to lack of complete product recovery.

Product Quality

The oils and chars were analysed at CANMET's Energy Research Laboratory in Ottawa. They were characterized using a battery of analyses commonly used to analyse synthetic fuels. Not all of the data is available, however elemental analyses are reported in Table 3.

The data in Table 3 indicate that, over the range of process conditions evaluated, the oil and char elemental analyses, with respect to end use, are not significantly different. Thus, while process conditions can affect product yield, it appears that product quality, with respect to elemental analysis, is relatively insensitive to process fluctuations.

Table 3. Oil and Char Elemental Analyses (%)

Run Number	OIL					CHAR				
	C	H	N	S	O	C	H	N	S	O
20	78.00	10.10	3.99	0.75	6.18	25.45	1.97	2.79	1.39	11.90
9	78.74	10.17	3.45	0.41	6.37	26.02	1.61	3.01	1.16	12.70
15	77.39	9.70	4.95	0.83	6.90	24.53	1.22	2.84	0.74	9.26
22	77.92	10.20	3.99	0.61	6.51	22.53	1.34	2.54	1.52	12.54
31	76.92	10.15	4.11	0.65	6.89	26.53	2.13	2.80	1.31	11.94
32	79.76	10.25	4.19	0.56	5.84	25.97	1.98	2.80	1.34	11.63
33	79.30	10.41	3.49	0.34	5.84	24.22	1.62	2.74	1.50	11.35

Rough elemental balances indicate that 40-45% of the carbon and 30-40% of the hydrogen are classified to the oil. However, only 3-6% of the oxygen, 10-15% of the sulphur and 20-30% of the nitrogen remain in the oil. All of the phosphorous and 75 to 85% of the sulphur remain in the char.

The oils were also analysed by sequential elution solvent chromatography to attempt to identify and quantify the constituents present. This analysis indicated that the oils contain approximately 26% saturated aliphatic hydrocarbons, ~3% monoaromatics, 1.93% diaromatics and 0.49% polyaromatics. Polar compounds, most likely carboxylic acids, accounted for 28%, whereas 0.9% was basic, pyridine

soluble matter, leaving about 39% unaccounted for. A breakdown of the aliphatic hydrocarbons is presented in Table 4.

Table 4. Aliphatic Hydrocarbon Distribution in Oil

Compound	%
C_{10}	8
C_{10-15}	30
C_{15-16}	6
C_{16-17}	5
C_{17-19}	10
C_{19-20}	10
C_{20-21}	10
$>C_{21}$	21
	100

Environmental Considerations

The environmental considerations that need to be addressed before such a process can be commercialized include the following:

(i) process emissions (both aqueous and atmospheric), and

(ii) The impact of product end use (oil, char, NCG).

These factors cannot be addressed adequately at this scale of operation, but some valuable information has been generated. Emissions from the process include the NCG and pyrolytic water. It is proposed that at full scale the NCG be combusted with the char to provide the heat needed to drive the process. Based on the limited data available, no new problems are foreseen in this respect. Metal balances indicate that all the metals remain in the char and, therefore, burning should produce an ash very similar to that generated via sludge incineration. It is anticipated that conventional air pollution control technology will be adequate.

The pyrolytic water produced does contain significant quantities of biodegradable material (approximately 10-15% organic carbons, essentially low molecular weight acids, etc.). Based on preliminary analysis, the concentrations of U.S. EPA priority pollutants in this stream are very low. Consequently, this stream appears suitable for high rate anaerobic treatment and this approach will be investigated.

The oil has as yet not been fully characterized with respect to priority pollutants. Metal analyses do indicate low levels (< 5 Mg/g) for metals such as Cu, Zn, Cr, V, Pb and Ni. The least valuable end-use for the oil would be to burn it as a fuel oil replacement and no undue environmental concerns are expected in this regard. However, the potential exists to increase end-use value, and upgrading to a transportation fuel will be investigated.

In general, at this point in time, no environmental constraints have been identified which would limit exploitation of the technology.

SUMMARY

Experiments conducted at the WTC, using a batch reactor system, have confirmed that Canadian sludges are amenable to conversion to liquid and solid fuels, using the technology developed by researchers from the University of Tubingen in West Germany. Oil yields of up to 25% appear to be readily achievable and thermal efficiencies of greater than 80% easily attained. The data generated on Canadian sludges has in essence confirmed the results generated by the German research and has indicated that this process appears superior to all others referenced in the literature. The most significant fact is that production of straight chain hydrocarbons end that published claims of net energies of 10-15 MJ/kg of dry sludge should be achievable for the thermal conversion process, provided mechanical dewatering of the sludge is practised (Bayer & Kutubbudin, 1982).

It is estimated that by 1985, 350 000 tonnes of sewage sludge will be incinerated annually in Canada. Thermal conversion of this sludge could produce 700 000 barrels of oil per year, with a market value of at least $28 million.

Studies are continuing at the WTC with the design, fabrication and testing of a 2.5 kg/h lab scale continuous

reactor system (Figure 3). The long term objective of the program is to demonstrate the process at full scale.

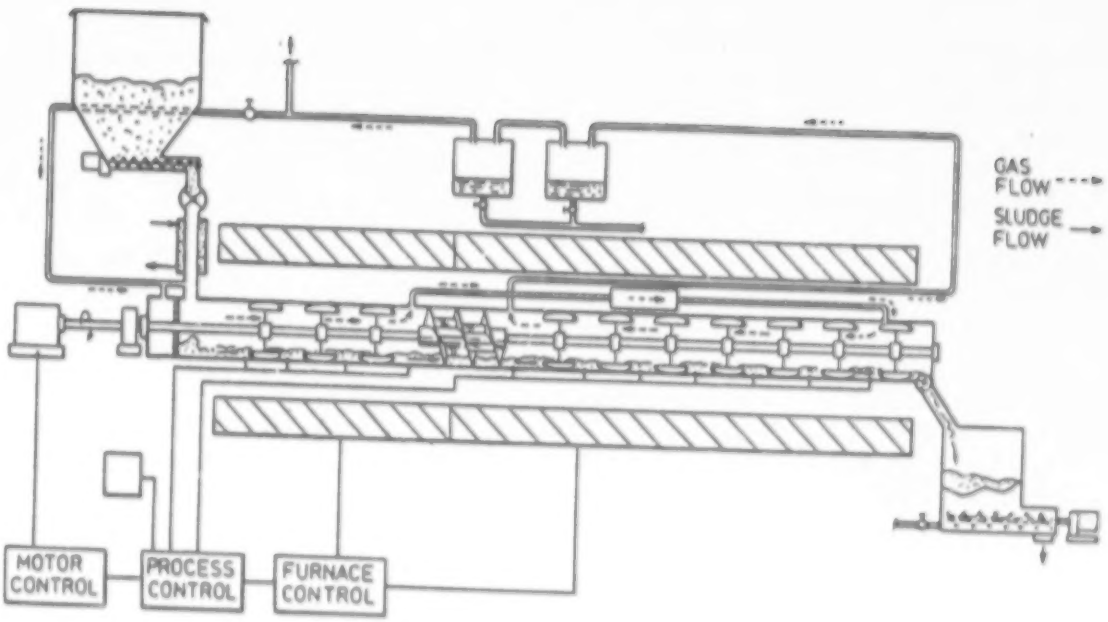

FIGURE 3. Continuous Laboratory Equipment

ACKNOWLEDGEMENT

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BIOMASS LIQUEFACTION PRODUCT ANALYSIS AND UPGRADING

DOUGLAS C. ELLIOTT AND ED G. BAKER
PACIFIC NORTHWEST LABORATORY
RICHLAND, WASHINGTON 99352
USA

INTRODUCTION

The products described were produced, for the most part, in the Comparative Test portion of the International Energy Agency, Forestry Energy Cooperative Project D-1 and as such are derived from two common feedstocks, a hybrid poplar wood from Canada and a peat from Finland. However, in two cases technical and financial problems precluded participation of research groups in the Comparative Test Program. From these research groups we have obtained representative products produced from feedstocks other than the two common feedstocks used by the Comparative Test participants.

The samples for analysis were provided by the participating laboratories. Generally, the samples were recovered from the experimental reactor systems without the use of solvents or other special handling procedures. The products were shipped in polyolefin or glass containers. No attempt was made to ship or keep samples under inert conditions. No product changes have been noted since receipt of the samples.

ANALYTICAL COMPARISONS

The program of analysis of products from the Comparative Test Program is now nearly completed. Ten laboratories in Canada, Sweden, Finland and the USA are participating in the program. Samples received very late in the program are still being analyzed. Detailed analyses will be included in the final report from the IEA cooperative project.

Based on our results, two general conclusions can be made about the products of direct liquefaction of biomass:

1) The pyrolysis products including supercritical extracted product, are a distinct group whose properties are greatly different from high pressure liquefaction products,

2) The difference in oil product from different species of wood is almost, but not entirely, undetectable, yet a peat-derived product is greatly different from the wood-derived material.

Specific examples of these differences are as stated below.

The pyrolysis products have:

- high oxygen and water contents and therefore a low energy density,
- very low insoluble solids and ash content due to the volatilization step in the processes,
- low temperature of thermal decomposition (as low as 170°C),
- little hydrocarbon extractable material,
- high miscibility with water making its removal difficult.

Conversely, the high pressure liquefaction products have:

- less oxygen and water and higher energy density than pyrolysis products,
- higher viscosity and pour point mainly as a result of less dissolved water,
- significant amounts of insoluble solids and ash,
- better thermal stability but a higher temperature distillation range,
- little actual hydrocarbon but significant aromatic character,
- immiscible water phase after distillation leading to facile separation.

Wood-derived liquefaction products generally have:

- higher oxygen and water contents and therefore lower energy density,
- lower solids and ash,
- very low sulfur and nitrogen contaminants,
- lower viscosity and pour point,
- lower hydrocarbon extractable material.

Peat-derived products, as a direct result of the feedstock properties, have:

- less oxygen and lower water solubility and higher energy density,
- more char or solids and more ash,
- 2% nitrogen and 0.2% sulfur,
- significant hydrocarbon content.

The peat pyrolysis products were actually solid at room temperature but their viscosity dropped more rapidly above their pour point than th wood-derived products.

BIOMASS LIQUIDS UPGRA G BY HYDROTREATING

Catalytic hydrotreating tests were performed with five different biomass liquefaction products, flash pyrolysis poplar oil, LBL and PERC oil produced from Douglas fir at the Albany Facility (TR7 and TR12 respectively) and two distillate oils from Albany products. Tnese were the only biomass products available in large enough quantities for these continuous-mode tests. Temperatures for the tests were generally from 300° to 350°C and pressures were between 13.3 and 16.8 MPa with residence times calculated at 10 to 20 minutes. Four different catalyst types were tested in this study including nickel metal, copper chromite, and cobalt-mobybdenum in both the oxide and sulfide form. Detailed data for the catalyst and feedstocks are shown in Tables 1 and 2 respectively.

Table 1. Catalyst Descriptions

Identifier	Cat. No	Manufacturer	Composition
CuCr	G22RS	United Catalysts	33.0% Cu, 27% Cr, 11% Ba, 1/8" tablet
Ni	Ni-1404	Harshaw	68% Ni on proprietary support, reduced and stabilized, 1/8" tablet
CoMo	CoMo-0402	Harshaw	3% Co, 15% MoO_3 on silica-alumina, 1/8", 3/16", 1/4" tablet
HT	HT-400	Harshaw	3% CoO, 15% MoO_3 on alumina, 1/8" extrusion

Table 2 Feedstock Descriptions

Feedstock	Percent Composition C	H	O	Moisture	Density	H/C Atomic Ratio	Viscosity @ 40°C
TR8 Trap Out Tray Oil	81.8	8.6	9.7	0.0	1.05	1.25	50 cps
TR7/TR12 Distillate	76.2	8.9	14.9	2.33			
(dry)	(78.0)	(8.8)	(13.2)	(0.0)		(1.34)	
Flash Pyrolysis Poplar	48.2	7.1	41.4	24.3	1.11		40 cps
(dry)	(65.9)	(6.1)	(28.0)	(0.0)		(1.10)	
TR7	72.3	8.6	17.6	8.5	1.12		70,000 cps
(dry)	(80.2)	(8.5)	(11.1)	(0.0)		(1.26)	
TR12	76.1	10.5	15.1	7.3	1.11		200,000 cps
(dry)	(80.6)	(10.3)	(9.1)	(0.0)		(1.52)	

The low viscosity PERC distillate oil, TR8 Trap Out Tray Oil was used as the common feedstock for the series of comparative catalyst tests. Table 3 contains the relevant operating data and product descriptions for these tests. The results clearly show the high activity of the nickel catalyst for both hydrodeoxygenation and saturation of the aromatic systems. Methane formation was also significant early in the run. The product is a light yellow liquid whose

Table 3. Hydrotreating Catalyst Comparative Tests With TR8 Trap Out Tray Oil

	Nickel a	Nickel b	Sulfided CoMo a	Sulfided CoMo b	CoMo a	CoMo b	Copper Chromite a	Copper Chromite b
Temperature, °C	347	284	358	300	355	343	327	315
Pressure, MPa	16.0	15.9	14.1	14.0	14.0	13.9	14.4	13.3
Oil Feed Rate, ml/hr	186	186	225	277	240	240	672	246
Hydrogen Feed Rate, ℓ/hr	271	271	206	206	162	30	305	305
LHSV, vol. oil/vol. cat./hr	0.22	0.22	0.23	0.29	0.27	0.27	0.75	0.27
Calculated Residence Time, hr	0.16	0.16	0.20	0.20	0.24	1.4	0.14	0.16
Hydrogen Consumption, ℓ/ℓ oil	695		276		96		-	
" " , SCF/bbl	3900		1550		540		-	
Carbon Conversion, wt%								
to Gas	5.3		0.4		0.4		0.2	
to Coke on Catalyst	18.9		10.9		13.1		8.3	
to Liquid Product	74		87		85.5		87.5	
Overall Carbon Balance	98%		98%		99%		96%	
H/C Ratio of Product	1.95	2.08	1.62	1.44	1.30	1.33	1.46	1.41
O Content of Product, wt%	1.1	1.5	2.0	2.4	7.7	7.3	8.5	9.5
Other Analyses	45.1 MJ/kg		532 ppm S					

a and b indicate two subsets of data from one continuous test.

Operating conditions were changed during the runs as presented in the Table.

These parameter changes had only minor effects on the product quality as indicated in the Table.

analysis by GCMS indicates the presence of mostly cyclohexanes. The infrared spectrum shows strong alkane bands with nearly total elimination of hydroxyl, carbonyl and aromatic bands. The sulfided cobalt-molybdenum catalyst is nearly as efficient in oxygen removal but results in much less hydrogen consumption due to the lesser degree of saturation of the aromatic components. Methane generation was almost nil. The copper chromite catalyzed some hydrogenation but almost no deoxygenation occurred and the unsulfided cobalt-molybdenum showed only slight activity for each reaction. These results correlate very well with earlier hydrotreating experience with phenolics (Elliott, 1983).

Carbon laydown on the catalyst is significant in all cases; however, no conclusion can yet be drawn as to this effect on catalytic activity. The sulfided CoMo exhibited slightly less carbon laydown than the unsulfided form and the nickel catalyst had the greatest degree of laydown. The fact that methane production with the nickel catalyst occurred primarily early in the test and may have subsided as a result of the catalyst becoming coked should be investigated further. Like the methane formation, the high carbon laydown percentage may merely be a phenomenon of the start-up of the nickel catalyst in this system. But this is only speculation, and for the present the data indicates that the combination of high carbon laydown and methane formation with the nickel catalyst results in a significant reduction in liquid product yield.

Table 4 is a listing of similar data for hydrotreating tests with the different feedstocks. Several important differences between the test with the TR7-12 distillate and the TR8 Trap Out Tray Oil can be seen. There is a larger carbon laydown on the catalyst with the TR7-12.

Table 4 Conditions and Results for Hydrotreating Biomass Liquefaction Products

	TR7-12 Distillate Sulfided CoMo 0402	TR7 Oil Sulfided HT400	TR7 Oil Ni-1404	Flash Pyrolysis Poplar Sulfided CoMo 0402
Temperature, °C	344	345	333	355
Pressure, MPa	13.6	16.8	16.3	13.8
Oil Feed Rate, ml/hr.	342	204	274	377
Hydrogen Feed Rate, ℓ/hr.	137	120	300	120
LHSV, vol. oil/vol. cat./hr.	0.38	0.24	0.30	0.35
Calculated Residence Time, hr.	0.24	0.35	0.17	0.24
Hydrogen Consumption, ℓ/ℓ oil	178	300/100	538	127
" " , SCF/bbl	999	1700/550	3271	713
Carbon Conversion, wt%				
to Gas	1.0	2	15	20
to Coke on Catalyst	19	8	9	60*
to Liquid Product	70	77	69	23
Overall Carbon Balance	90	87	93	103
H/C Ratio of Product	1.72	1.75/1.40	1.82	1.55/1.45
Oxygen Content of Product, %	2.2	0.8/4.6	5.3	3.6/5.9
Sulfur Content of Product, ppm	--	441/214	--	--

*The catalyst bed was nearly full of a coke material.

Two possible explanations for this difference may be the lower hydrogen partial pressure in the reactor due to the lower operating pressure and lower hydrogen to oil feed ratio, or the difference in feed material since the Trap Out Oil is essentially a 35% distillate while the TR7-12 distillate represents closer to 50% of the whole oil. The coke formation on the catalyst may be the key to explaining the low hydrogen consumption with the TR7-12 distillate. Hydrogen gas formation at the time of coke formation may explain the apparently lesser consumption of hydrogen to transform the heavier, more oxygenated TR7-12 distillate to a more hydrogenated product. The slightly longer residence time may have contributed to the better product quality.

The two tests with the TR7 whole oil again demonstrate the difference in activity of the two catalysts. The nickel catalyzed test resulted in high hydrogen

consumption and saturation of aromatic components (as demonstrated by infrared spectrophotometry). Higher hydrogen flow was required to maintain an excess of hydrogen in the system. High methane formation was evident, but carbon laydown on the catalyst was lower when compared with the distillate product. The increased operating pressure may be a partial explanation for both of these observations.

When operating with the sulfided cobalt-molybdenum catalyst two different products were produced. Early in the run a relatively high quality product was produced that appears to be similar to the product resulting from the distillate hydrotreating tests. This product was followed in time by a second, lower quality product which was similar to the product produced with the nickel catalyst in terms of oxygen content but had a much lower level of hydrogen saturation of aromatics. There is, as yet, no well-founded explanation for this duo-product production; however, as of this writing the reactor system has been modified from up-flow to down-flow through the catalyst bed in order to perform additional tests to address the question.

A single test with TR12 oil was attempted in the down-flow mode. Even with the product preheated to 71°C the material could not be pumped consistently through the reactor system. Reactor and/or pump modifications are required in order to hydrotreat the material in the experimental reactor system.

A single test with the flash pyrolysis product was entirely unsatisfactory. Plugging occurred in the process lines downstream from the reactor and in the back-pressure regulator. The two product descriptions in Table 4 are for product materials collected before and after a first plugging incident. The test was discontinued after a second stoppage of flow. Upon opening the reactor afterward, the catalyst bed was found to be solidly encased in a brittle, coke material which had to be chipped out of the reactor. This material was apparently formed by the thermal decomposition of the feedstock which proceeded at a faster rate than the hydrogenation reaction. The solid would not melt, just as the residue of vacuum distillation of the feedstock would not. However, the oxygen content of the distillation resid was much higher (34%) than the solid coke (15%).

In consideration of the potential of hydrotreating only the distillate from flash pyrolyzate, thermal stability tests on the whole oil and a distillate were performed. The distillate, representing 39% of the organic material or 54% of the total product, was an orange-colored, low viscosity liquid before the test. Both liquids were sealed in high pressure autoclaves. The autoclaves were purged with nitrogen, sealed, and heated to 270°C where the temperature was held for thirty minutes before cooling. In both cases, the recovered materials were composed of a brown-colored aqueous phase and a solid char. This compares with a similar test of the Albany product TR7 in which little detectable change in the oil was noted after the same treatment.

The conclusions from these tests are that the high-pressure biomass liquefaction products are more amenable to catalytic hydrotreatment using commercially available hydrodeoxygenation catalysts than simple pyrolysis products. Distillates can be converted to gasoline-like hydrocarbons at commonly acceptable conditions of temperature, pressure and residence time. The whole oils can also be hydrotreated but product quality is not so good and further process optimization is required to achieve production of products of transportation fuel quality. Flash pyrolyzate oil produced from poplar is too thermally unstable to be treated at the same conditions as the high-pressure products. More active catalysts which can operate at lower temperatures and can out-strip the thermal decomposition reactions are needed if hydrotreatment of such products is to be feasible. Due to its large amount of light components (less than five carbons) hydrotreatment of pyrolysis products to produce liquids will always operate from a starting disadvantage since these components would not produce liquids except through some type of condensation reaction.

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CHEMICAL STUDY OF THE LIQUEFACTION OILS FROM POPLAR WOOD

by

N. Soyer, C. Fredon, C. Bruneau, A. Brault.

Laboratoire de Chimie Organique et de l'Environnement - Ecole Nationale Supérieure de Chimie de Rennes, Avenue du Général Leclerc - 35000 Rennes - Beaulieu (France).

At the Ecole Nationale Supérieure de Chimie de Rennes, we have been working on direct liquefaction of biomass since 1980. Our purpose was to design simple experimental conditions to produce liquid fuel from poplar wood. Using a procedure similar to that described by Boocock et al. (1980, 1982), the influence of the main parameters on oil yield and its chemical composition have been studied (Fredon 1983 and Fredon et al, 1983).

We aim at the definition of a standardized analytical procedure which has been recognized as an important objective by many others (Karlsson et al (1982), Schaleger et al (1982), Elliott (1982), Kallury et al (1982)).

RESULTS AND DISCUSSION

Production of oils

The oils studied were obtained by treating poplar sawdust (varieties: Robusta + I222) in the presence of water, at 350°C for 30 minutes, under an initial cold pressure of 7 MPa of hydrogen. The reaction was carried out in a one liter autoclave (AE). Among all the nickel catalysts tested (carbonate, acetate, acetylacetonate and activated nickels), the activated nickels especially Raney nickel gave the best results. Little amounts were used, comprising about 2.2 wt % of the anhydrous wood.

The total yield of liquid compounds was about 40 wt % Acetone Soluble. They consisted of oils 96% extractable with dichloromethane and the remaining 4 wt % were tar which was only soluble in acetone.

The chemical and physical properties of the oils were the following:

- elementary analysis, C: 72-73 %; H: 7.4-7.8%; O: 18-19 %
- calorific value: 32.5 MJ/kg
- viscosity: 1.0-1.3 X 10^{-3} m^2/s at 100°C.

Chemical analysis of the oils

Infrared and N.M.R. spectroscopy showed that all the anhydrous oils had similar spectra despite the different reaction conditions used in our experiments. The IR spectra depicted a broad absorption in the range of 2300-3700 cm^{-1} with a maximum at 3400 cm^{-1} which we assigned to the OH stretching vibration; another strong band at 1700 cm^{-1} was assigned to the C = O stretching vibration. This information suggested the presence of phenolic compounds, carboxylic acids and ketones in the oils. The proton NMR examination in $CDCl_3$ showed broad signals in the ζ 6-7.5 region assigned to aromatic and hydroxylic protons (20 to 25%), in the δ 1.7-3.5 region assigned to aliphatic protons and a singlet at 3.8 ppm corresponding to $O-CH_3$ group. The acidity of the oils was determined by measuring the pH in water ethanol (83 : 17). The acidity corresponded to a range of 0.7-1.0 H^+ milliequivalent per gram of crude oil.

GCMS with a capillary column was used for the analysis of the oils. On account of the low volatility of the sample and the stationary phase used (FFAP, up to 250°C), an important fraction of the oil cound not be analyzed (50-70 wt %). Only the identification of the main peaks of the chromatogram was attempted. C_5 and C_6 carbonyl compounds, C_2 to C_4 carboxylic acids, phenol (which gave the most important peak), alkylphenols, guaiacols and syringols were observed. In addition dihydroxybenzenes and related compounds were detected when the oil was derivatized by acetylation in the

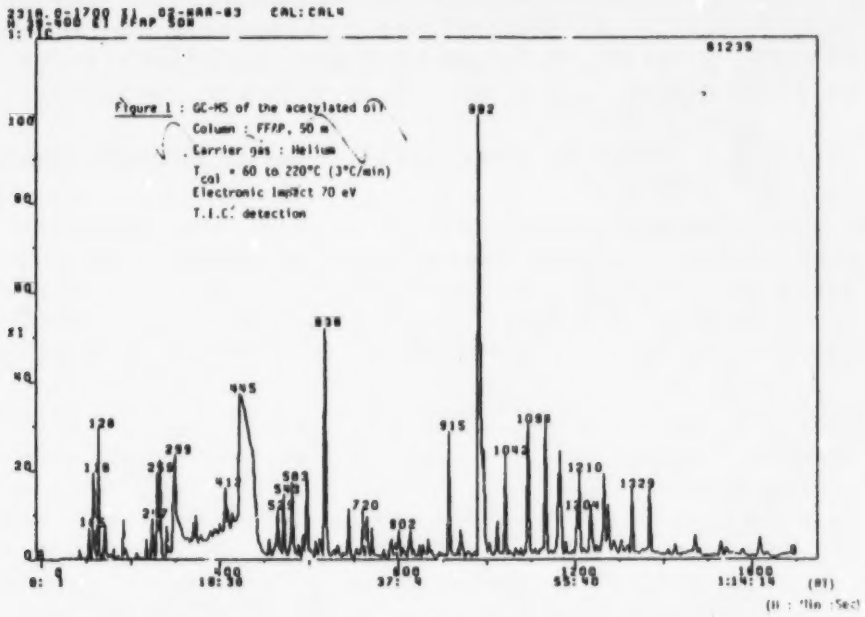
presence of 4-(dimethylamino) pyridine (Figure 1 and Table 1). The guaiacols, syringols, and alkylphenols were identified using the retention indices relative to the phenol which was present in all samples. A quantitative determination of phenol and cyclopentanone in the oils gave yields around 2.5 wt % and 1.7 wt % of crude oil respectively.

Table 1. Products Identified from an Acetylated Oil by GC-MS

Peak n°	Product	Peak n°	Product
105	Acetone	867	Propyl phenol
113	Tetrahydrofuranne	871	C_4 phenol
117	Ethanol	915	Guaiacol
120	Butanone	941	Biphenyle
140	Propanol	993	Methyl guaiacol
142	Pentanone-2	1025	Propenyl phenol
183	Butanol	1043	Ethyl guaiacol
189	Hexanone-2	1094	Dihydroxy benzene
260	Cyclopentanone	1133	Propenyl guaiacol
264	Methyl cyclopentanone	1160	Methyl dihydroxy benzene
281	Methyl cyclopentanone	1167	Syringol
346	Cyclohexanone	1204	Methyl dihydroxybenzene + propyl guaiacol
543	Methyl cyclopentenone		
634	Phenol	1211	Ethyl dihydroxy benzene
689	Cresol	1236	Methyl syringol
720	Cresol	1256	Propyl dihydroxy benzene
729	Cresol	1274	Ethyl syringol
742	Dimethyl phenol	1288	3-(4-Hydroxy-3-methoxy-phenyl)-1-propanol
767	Ethyl phenol	1329	Propyl syringol
782	Ethyl phenol	1368	Methoxy dihydroxy benzene
785	Ethyl phenol	1411	Methyl methoxy dihydroxy benzene
794	C_3 phenol	1471	Methyl methoxy dihydroxy benzene
802	Dimethyl phenol	1481	Propenyl dihydroxy benzene
817	C_3 phenol	1529	Ethyl methoxy dihydroxy benzene
823	Dimethyl phenol	1617	Propyl methoxy dihydroxy benzene
847	C_3 phenol		
856	Dimethyl phenol		

On account of the complexity of the oils, some separations in groups of compounds were performed. A chemical separation obtained by successive extractions at controlled pH gave three fractions: phenolic, neutral and acid, the different yields of which were about 39, 22 and 11 wt % respectively. Important losses were attributable to this method (about 28 wt %); therefore we did not select it for systematic analyses. Gas phase chromatography & NMR showed that the neutral fraction consisted of essentially aliphatic compounds.

FIGURE 1. GC-MS of the acetylated Oil Column: FFAP, 50 m; Carrier gas: Helium; T = 60 to 220°C (3°C/min); Electronic Impact 70 eV; T.I.C. detection



Distillation under reduced pressure was also attempted. Fractions were collected each 20°C (Table 2).

Fraction	Eb°C /0.6 mm Hg	Weight %	Elementary analysis C %	H %	O %
1	<100	12.5	70.1	8.9	20.7
2	100-120	12.5	71.5	8.7	20.0
3	120-140	13.5	72.5	8.0	19.8
4	140-160	6.5	75.5	8.3	17.0
5	160-180	5	75.8	8.2	16.7
6	180-200	4.5	75.7	8.1	16.5
7	200-240	11	76.1	7.7	16.7
residue	---	34.5	--	-	--

I.R. and N.M.R. spectra of the fracitons were very similar to those of the crude oil and gave no additional information. Only the first four fractions could be analyzed by gas chromatography.

Liquid phase chromatography was performed with a silica gel column as the stationary phase and three fractions were collected by successive elution with dichloromethane, acetone and methanol. The yield of the first fraction varied between 30 and 50 wt % of crude oil, depending on the volume of dichloromethane used. The corresponding mixture could be analyzed by gas chromatography-mass spectrometry (Figure 2).

After the elution of many light compounds (retention indices relative to the phenol < 0.7), the phenols were eluted according to the following sequence: guaiacols, phenol, alkylphenols, syringols. The cyclic ketones and the carboxylic acids were detected in a region located between the alkylphenols and the syringols. At the end of the elution, two major compounds were detected but they were not identified. The second fraction obtained by elution with acetone (45-70 wt %) contained compounds which were not eluted by gas chromatography in our conditions. They probably consisted of fragments of lignin partially degraded. We are now trying to analyze this polar fraction by means of adsorption and permeation chromatography to have an idea of the number of components and to identify them if possible.

The fraction eluted with methanol (about 10 wt %) consisted of a resinous mixture.

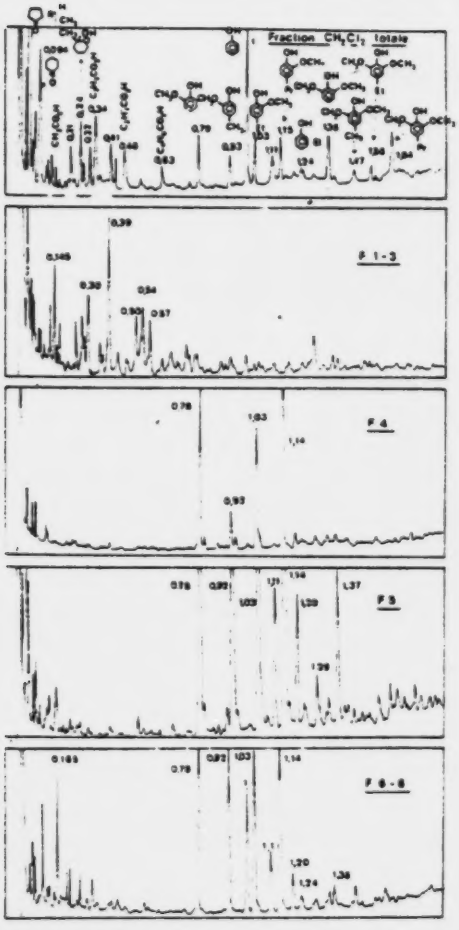


FIGURE 2a.
Chromatographic analysis of the different fractions eluted by CH_2Cl_2 (F1 to F25); 1 F = 60 m) Column:CW-20 M, L = 10 m., I.D. = 0,2 mm. Tinj. = Tdet. = 275°C; Tcol. = 6- to 200°C (6°C/min). Carrier gas: N_2

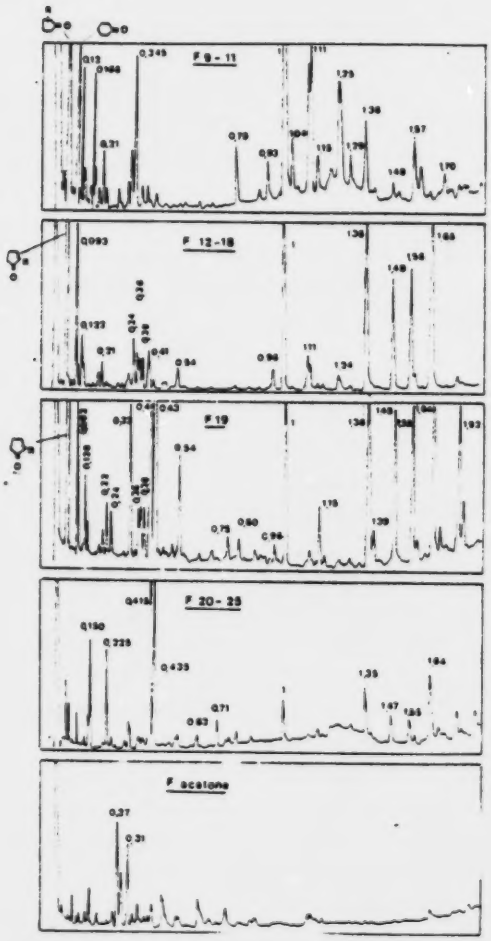


FIGURE 2b

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- CEMAGREF (Parc de Tourvoie, 92160 Antony, France)
- TOTAL (C.F.P., 5, rue Michel-Ange, 75016 Paris, France).

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RAPID CHARACTERIZATION OF PYROLYSIS OILS BY FLASH VOLATILIZATION AND MOLECULAR-BEAM SAMPLING/MASS SPECTROMETRY

R.J. Evans, M.N. Soltys, T.A. Milne
Solar Energy Research Institute
1617 Cole Blvd, Golden, CO 80401 U.S.A.

INTRODUCTION

Characterization of pyrolysis oils by conventional analytical methods such as liquid and gas chromatography, GC/MS, and spectroscopic techniques are generally time consuming and result in a wealth of information due to the complex nature of the sample. These results must be reduced to some easily interpretable form for overall comparisons of oils to be made. Mass spectral "finger-prints" of pyrolysis oils have been collected with the objective of designing a rapid, qualitative process which will allow a broad classification of oils, but still give some clues to the mechanisms and specific end products associated with each process.

The fast pyrolysis/molecular-beam sampling/mass spectrometer (Figure 1) in use at the Solar Energy Research Institute for the study of fundamental pyrolysis processes

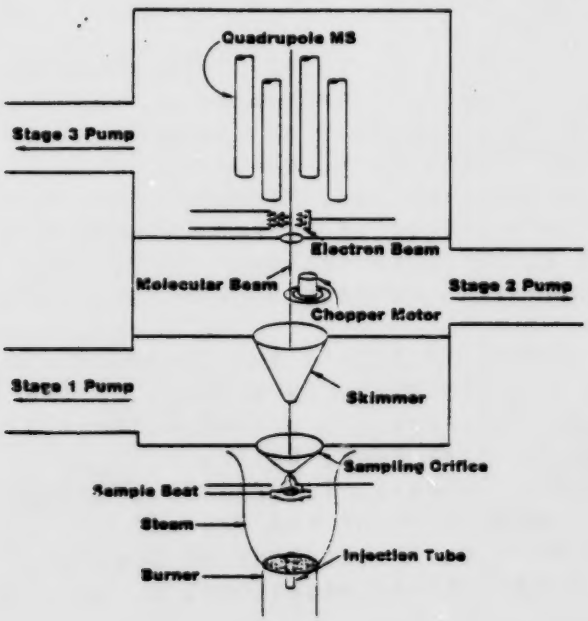

FIGURE 1. Molecular-Beam Apparatus for Fast Biomass Pyrolysis

has several characteristics which are useful as a tool for analytical pyrolysis as well. Two recent papers (Milne, T.A. and Soltys, M.N., 1983a and 1983b) have described the technique in depth and give examples of its basic applications. The system as shown in Figure 1 is run by suspending a quartz boat of oil or biomass(25-50 mg) in the unignited flame gases (H_2, O_2, and He) and positioned at 5 mm below the sampling orifice. At this position, residence time (≈5-25 ms) is insufficient for secondary cracking to occur. The flame is ignited and the 900°C steam and helium, which are maintained free of oxygen, heat the sample to either volatilization in the case of oils or to pyrolysis for feedstock characterization. Since both processes are endothermic and essentially ablative, the actual process temperature is well below the 900°C steam/He (Milne, T.A. 1983a). The sonic sampling orifice rapidly quenches the sampled gases which are subsequently collimated as a molecular beam for introduction into the ion source of a quadrupole mass spectrometer. Low electron energy impact ionization (15.5 eV) is used to minimize fragmentation.

The free-jet expansion of the sampled gases results in rapid quenching and presents internally cooled molecules to the ion source which also minimizes ionization fragmentation. Collimation yields a beam which contains both volatile and condensible species and therefore allows a unique look at the primary products of pyrolysis.

The two major disadvantages of the technique are: difficulty in quantitation due to mass discrimination in the molecular beam and variation in ionization sensitivities; and the ambiguity in structure assignment based on only the ion mass. Nevertheless, much information can be gained with tentative identification especially when different samples or treatments are compared.

The primary pyrolysis products of cellulose are shown in the top of Figure 2. The spectra is dominated by levoglucosan (162), which also makes major contributions to masses 60, 73, 98, and 144 due to ionization fragmentation. The dimer of levoglucosan (324) and fragments of higher polymers at masses 325, 234, and 163 dominate the higher-molecular-weight range. The furan compounds are the other major products from cellulose at 98, 110, and 126.

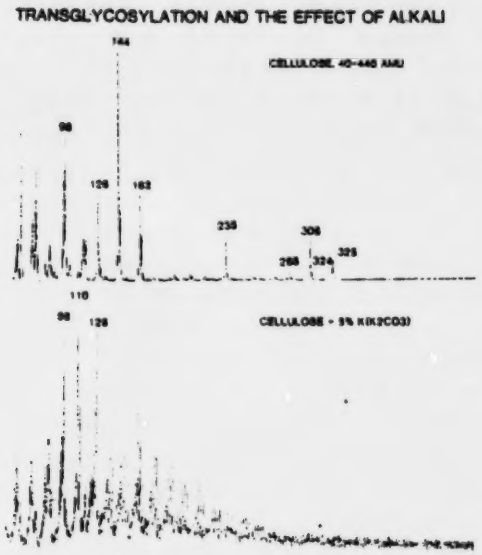

FIGURE 2. Low Voltage Mass Spectra of the Primary Pyrolysis Products of Cellulose (top) and Cellulose Treated with 5% (mole) K^+.

As an example of how this technique can show detailed differences in pyrolysis, the spectra of cellulose treated with 5% (mole) K as K_2CO_3 (≈1% wt K) is shown in the bottom of Figure 2. The treatment prevents the formation of levo-glucosan and the spectra is dominated by the furan compounds and a complex array of high-molecular-weight condensation products probably due to chain crosslinking.

In order to test this technique as a "fingerprinting" technique, samples of representative pyrolysis oils and liquefaction products, along with a sample of the feedstock, were requested from workers in the field. The pyrolysis of the feedstock in 900°C steam/He and molecular-beam sampling of the primary products was then compared with the spectra of the volatilized oil sample to see the effect of the liquefaction process on the composition of the resulting oil.

RESULTS AND DISCUSSION

A possible problem with the volatilization of the oils in 900°C steam/He is that the oils will be further cracked or undergo condensation reactions. Less than 3% of the oil remains as residue, which is a good indication that these problems are not of major concern, but this is a major unknown factor in this interpretation.

Based on the results presented here, four classes of oils have been assigned: primary oils (e.g., vacuum pyrolysis and supercritical extraction oils); slightly cracked oils (e.g., entrained-flow and updraft gasifiers); highly-condensed oils (e.g., high-pressure catalytically-assisted oils); and highly-cracked oils (e.g., downdraft gasifier and fast pyrolysis oils). Each group will be discussed in turn.

Group 1 - Primary Oils.

The vacuum pyrolysis process of Roy et al. (1982) produces a distribution of products which closely resembles the primary products as determined by this technique. A comparison of the two spectra for whole aspen wood is shown in Figure 3. In the directly observed spectra of the aspen (top) the major peaks are from lignin and due to coniferyl alcohol (180) and sinapyl alcohol (210), the two basic building blocks of hardwood lignin. In the flash volatilization of Roy's vacuum pyrolysis from the same sample these two peaks are no longer dominant with the major peaks switching to the lighter syringyl products at 154 and 168. This may be due to the extended thermal treatment even in vacuo or perhaps to cracking during the revolatilization step. The cellulose contribution is best estimated by the 124 (guaicol) to 126 (hydroxymethyl furfural) ratio. This shows more of a cellulose contribution in the directly observed sample although there are more lower-molecular-weight cellulose pyrolysis peaks (57,60,85,98) in the vacuum pyrolysis sample.

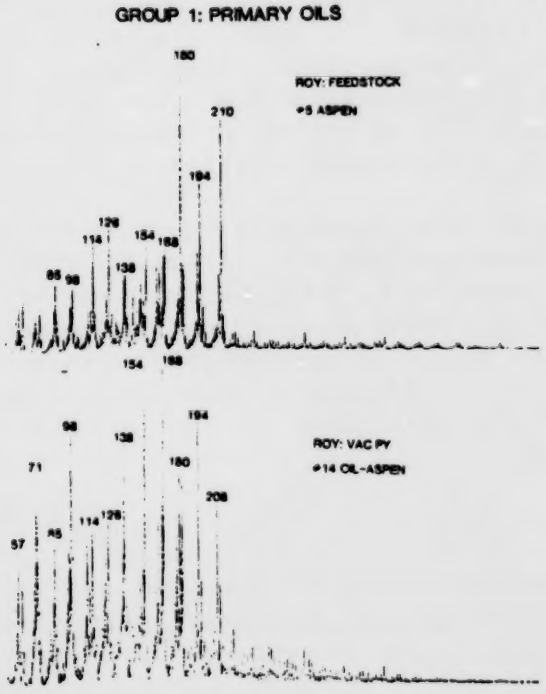

FIGURE 3. Mass Spectra of the Vacuum Pyrolysis Oil (Roy) Derived from Whole Aspen Wood (Bottom) and the Primary Pyrolysis of the Feedstock from which it was Derived (Top).

The comparison of the extractive-free aspen wood spectra shows an unexpected result of the extraction process. Although the fast pyrolysis spectra (Figure 4, top) is virtually identical to that for the whole aspen shown in Figure 3 (top), the vacuum pyrolysis spectra (Figure 4, bottom) is significantly different from the whole wood vacuum pyrolysis oil. The carbohydrate contribution is much greater in this sample as shown by the 124/126 ratio and particularly by the elevated intensity of 144 and 73 which are key levoglucosan fragment ions. Perhaps the extraction process removed some alkali which was inhibiting transglycosylation, although it is not clear why this effect was not noticed in the fast pyrolysis results.

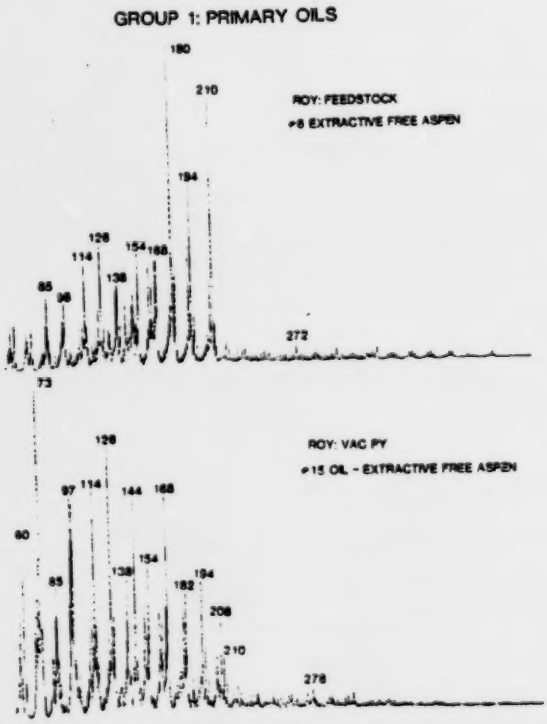

FIGURE 4. Mass Spectra of the Vacuum Pyrolysis Oil (Roy) Derived from Extractive-Free Aspen (bottom) and the Primary Pyrolysis of the Feedstock from which it was Derived (Top).

Figure 5 shows a comparison of the pyrolysis of lignin, which was separated by steam explosion. The similarities here are great with 180 and 210 of diminished importance in the separated sample.

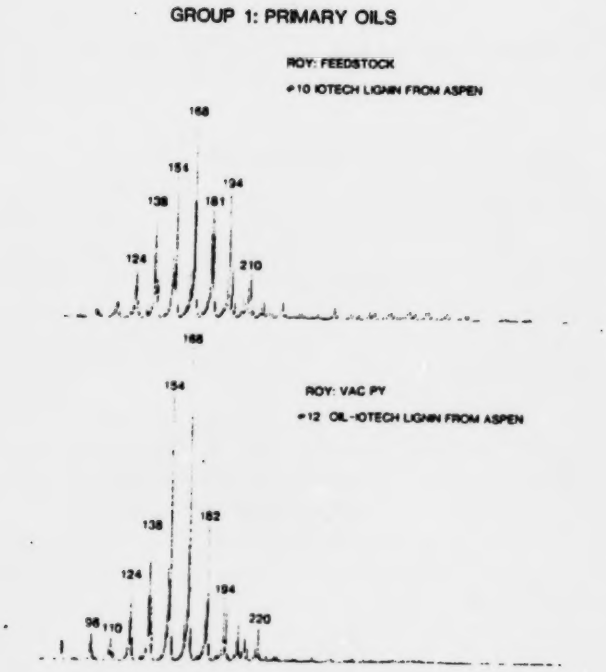

FIGURE 5. Mass Spectra of the Vacuum Pyrolysis Oil (Roy) Derived from Iotech Aspen Lignin (bottom) and the Primary Pyrolysis of the Feedstock from which it was Derived (top).

Figure 6 shows spectra of the oil produced by Kaliaguine by supercritical methanol extraction of aspen wood. The oil from a low temperature treatment is shown at the bottom and the lignin peaks predominate although 180 and 210 are decreased in intensity as was found in the vacuum pyrolysis oil. Several new masses appear in this scan, which are difficult to explain--the peak at 112, the odd mass at 149, and the series at 167, 279, and 391 separated by 112 mass units. Masses 167 and 149 are 18 amu apart as are the cellulose peaks 144 and 162, which are missing here. The higher temperature oil (top) shows a significant contribution from the cellulose peaks at 60, 73, 85, 98, and 126. The odd masses are still present and the spectrum is more complex at higher molecular weight.

GROUP 1: PRIMARY OILS

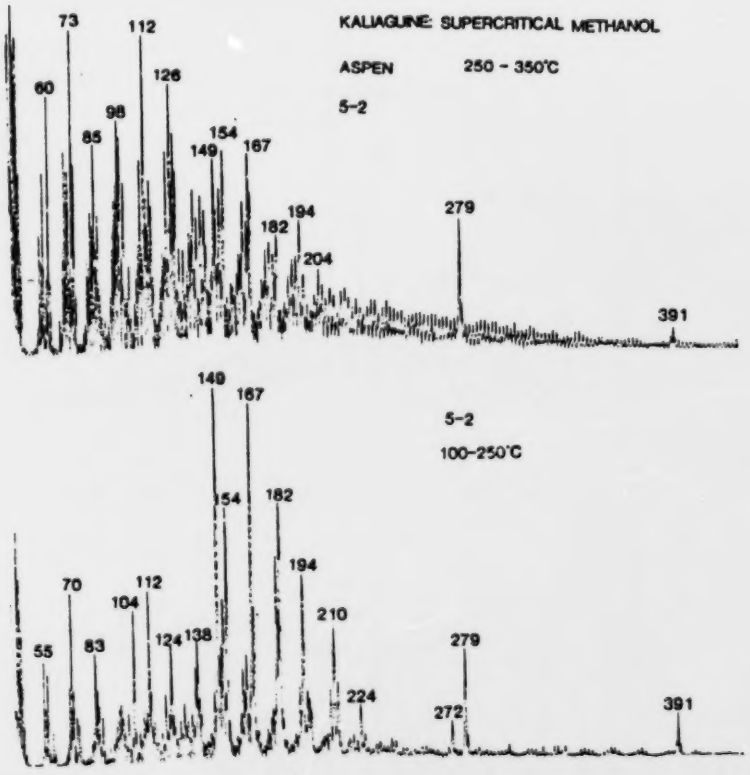

FIGURE 6. Mass Spectra of Oils Produced by Supercritical Methanol Extraction of Aspen at Low (bottom) and High (top) Temperatures (Kaliaguine).

In Figure 7 the supercritical tetrahydrofuran extraction oil spectra from aspen are shown at the same two temperatures. The lignin peaks still predominate at low temperature but the differences from methanol are great: mass 112 is missing, a different odd mass series (177, 265, 353) is present separated by 88 amu (this series is missing entirely at the higher temperature), and the cellulose peaks are not present at the higher temperature.

Group 2 - Slightly Cracked Oils.

These oils are from processes designed to produce liquids, but have slightly longer residence times than

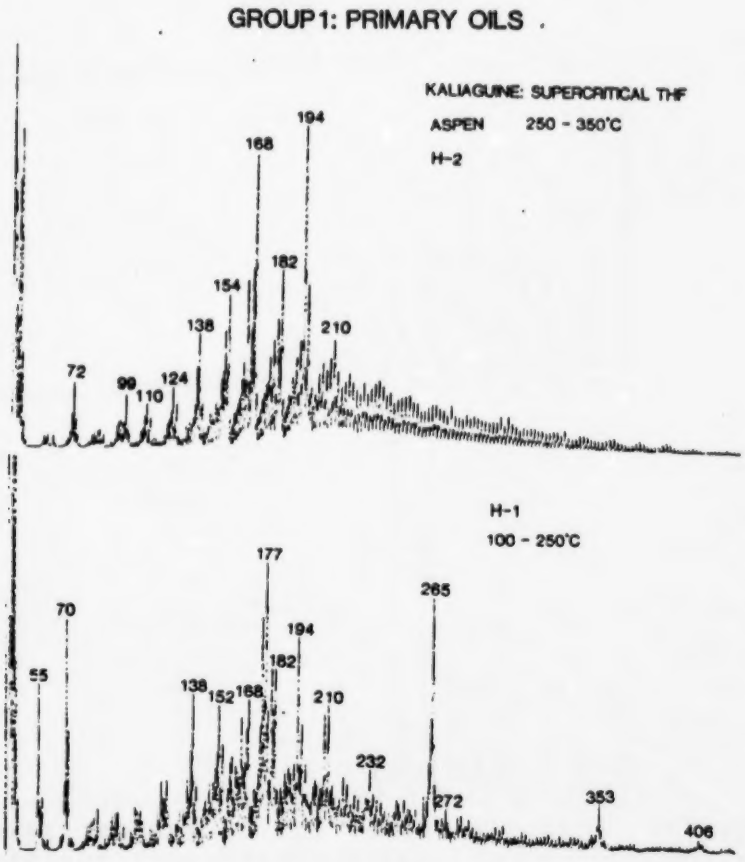

FIGURE 7. Mass Spectra of Oils Produced by Supercritical Tetrahydrofuran Extraction of Aspen at Low (bottom) and High (top) Temperatures (Kaliaguine).

primary oils. In Figure 8 are shown two different fractions from one run in the entrained-flow pyrolysis system of Knight at the Georgia Institute of Technology. The first sample (sump 1) shows contributions from both cellulose (60, 73, 88, 98, 126, 144) and lignin (110, 124, 138, 154, 182, 196, 210). The samples from later collection points (sump 4) shown only lignin peaks and with a different distribution from the first sample. The carbohydrate products may have been selectively cracked by the time sump 4 was condensed as well as the more labile lignin peaks.

Another slightly cracked oil is from Soltes at Texas A & M using a modified updraft gasifier to produce tar.

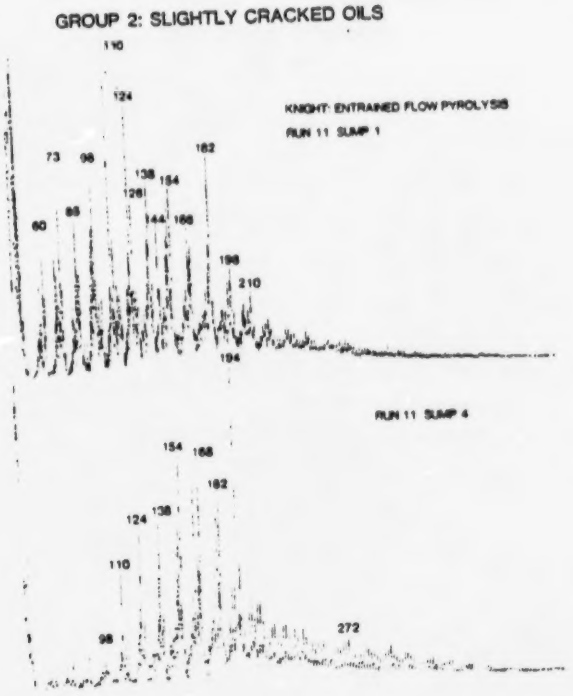

FIGURE 8. Mass Spectra of Oils Produced by the Entrained-Flow Pyrolysis of Wood Oil Samples from Two Different Collection Points (Knight).

The fast pyrolysis of the pine feedstock is shown in Figure 9 This is typical of softwoods with 180 (coniferyl alcohol), the base peak, and an additional set of lignin peaks at higher molecular weights (272-326). There is a limited carbohydrate contribution in this spectrum. The bottom spectrum of Soltes' tar shows the degree of cracking with the higher-molecular-weight components selectively removed; 180 has been reduced to a minor peak and increased proportions of the lower-molecular-weight guaicol series (110, 124, 138) are observed.

The pyrolysis of rice hull feedstock under these same conditions shows this effect even more. The fast

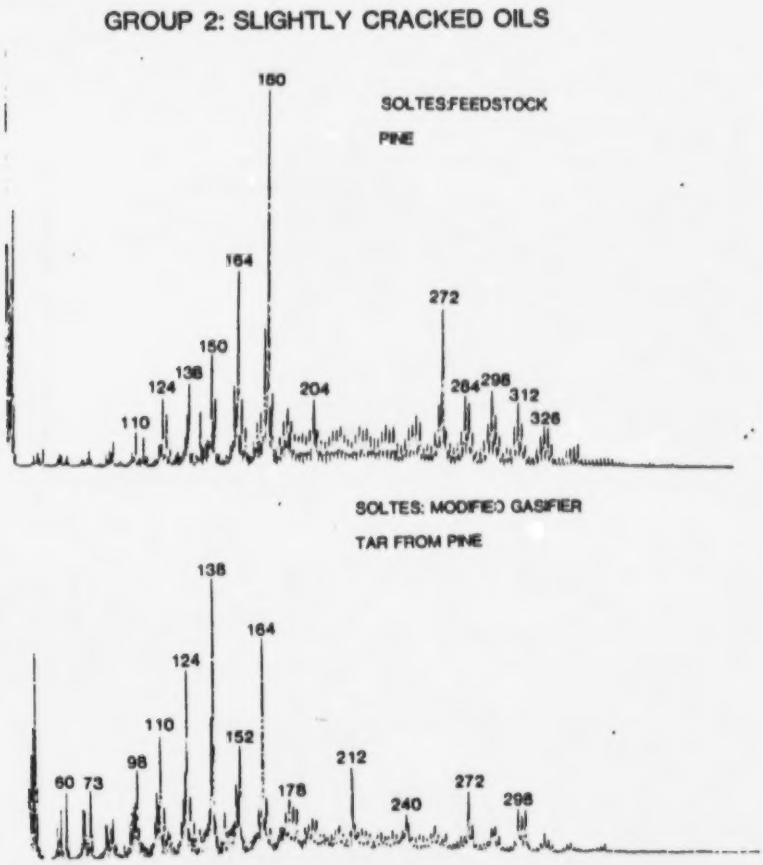

FIGURE 9. Mass Spectra of the Modified Gasifier Tar (Soltes) Derived from Pine and the Primary Pyrolysis of the Feedstock from which it was Derived.

pyrolysis spectra is shown in the top of Figure 10. A new peak is observed at mass 120 which may be derived from the coumaryl alcohol lignin monomer (150) with mass 120 being 4-vinyl phenol. This peak at 120 is also found in corn cobs. There is a large input from cellulose (126) and hemicellulose (114) in addition to the lignins. The tar spectrum (bottom) shows a complete alteration of the primary products with the formation of phenol (94), cresol (108), and an unknown at mass 122. The remaining peaks are more complicated than a lignin spectrum and could be due to the presence of condensed aromatic species such as acenaphthalene (152) and anthracene (178), although this is speculative.

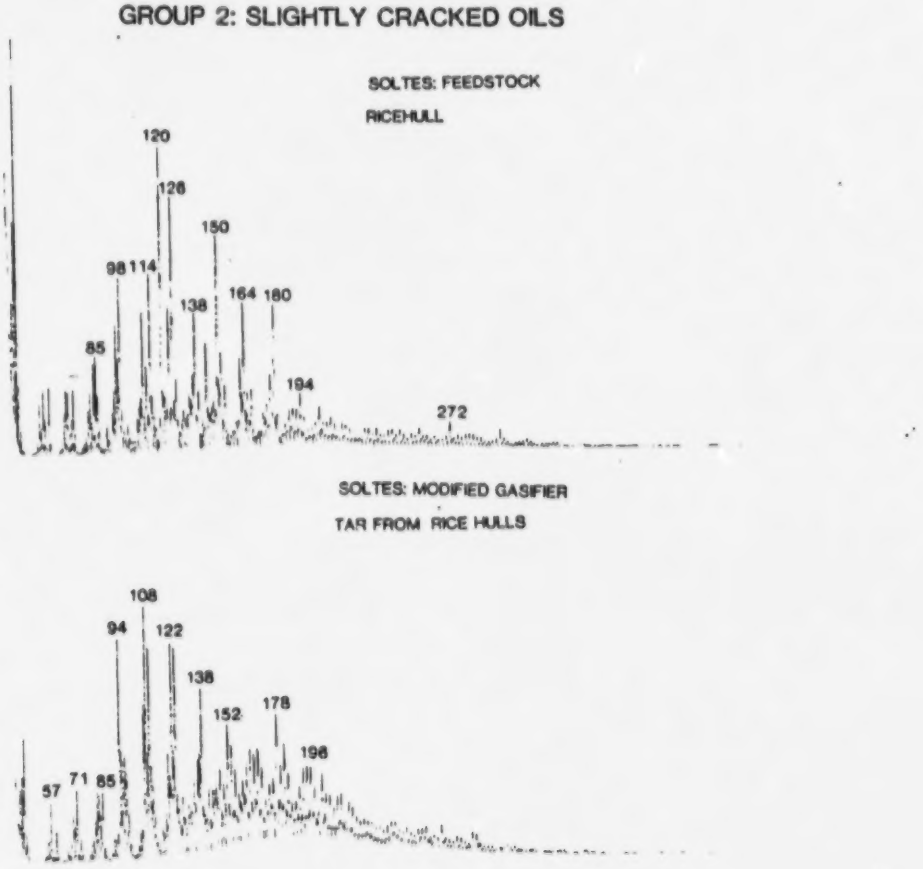

FIGURE 10. Mass Spectra of the Modified Gasifier Tar (Soltes) Derived from Rice Hull (bottom) and the Primary Pyrolysis of the Feedstock from which it was Derived (top)..

Group 3 - Condensed Oils.

The oils and tars in this group are formed in a qualitatively different way, being the product of more prolonged heating under high pressure and in the presence of alkali catalysts. In Figure 11 are shown the fast pyrolysis spectra of the fir feedstock (top) and the spectrum of the Albany tar obtained from Elliott. The feedstock shows the typical softwood distribution with coniferyl alcohol (180), the base peak, and a reasonable contribution from cellulose with the presence of the levoglucosan dimer at 324 and 325, which is rare in wood samples. The Albany process completely changes the distribution of pyrolysis products. Some lignin peaks may still be present (150, 164) but structure assignment where the product slate has changed so much and the spectrum is so rich is a questionable practice. Condensed aromatic structures are probably the main products.

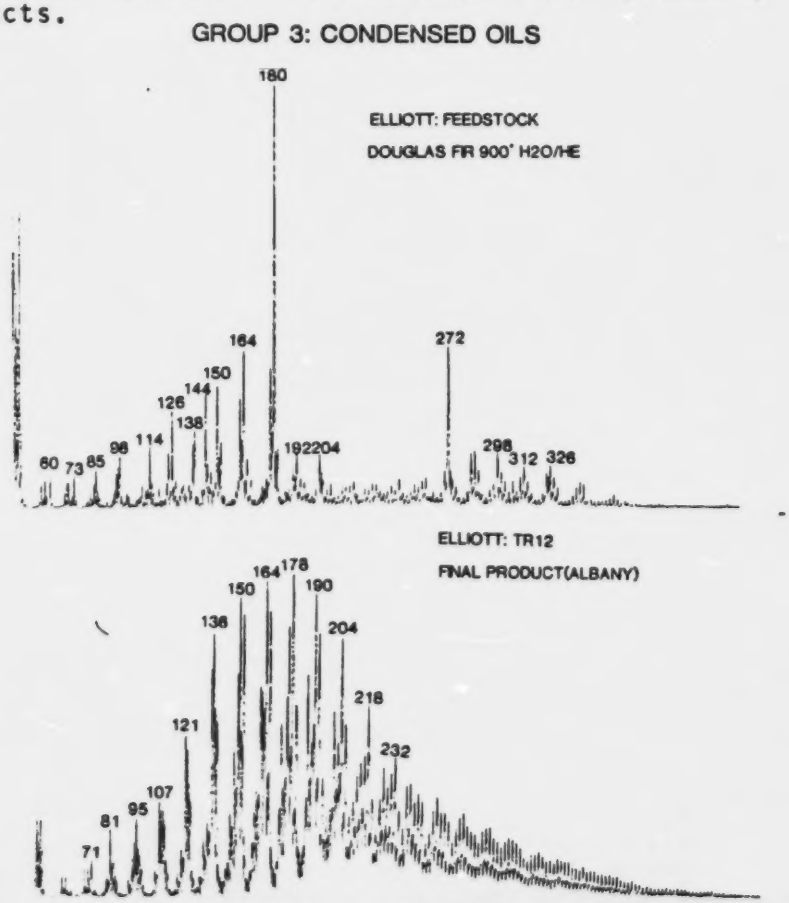

FIGURE 11. Mass Spectra of the Albany Product (Elliott) produced from Fir Wood (bottom) and the Primary Pyrolysis of the Feedstock from which it was Derived (top).

In Figure 12 a sample derived from cellulose by the same type of process is shown along with the fast pyrolysis spectrum of the feedstock. Some differences exist between the cellulose spectra in Figures 2 and 12. The increase in 126 relative to 144 and the increased complexity of the higher mass region indicate the presence of a trace of alkali in this sample. The presence of 114 also indicates some hemicellulose constituents which are present. No lignin is indicated by the spectrum, however. The process oil spectrum is striking in that it is completely dominated by aromatic compounds although 110 may be in part due to cellulose derived 5-methylfurfural. The 124, 138, 150, 164 resemble the guaicol series and 178, 192, and 204 are probably the poly-nuclear aromatics.

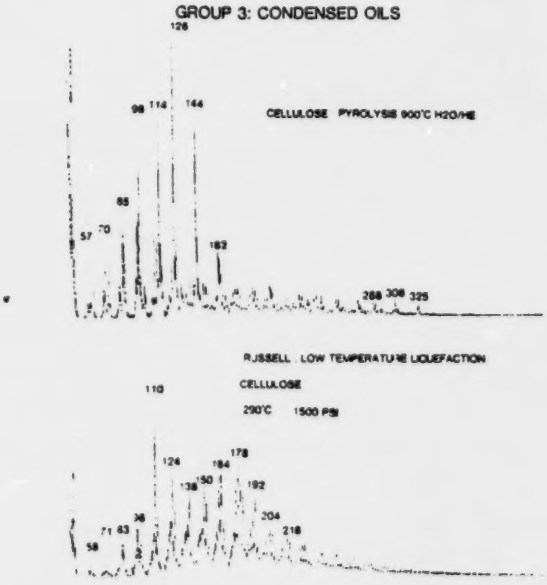

FIGURE 12. Mass Spectra of the Oil Derived from the High Pressure Alkali Catalyzed Pyrolysis of Cellulose (Russell) (bottom) on the Primary Pyrolysis of the Feedstock from which it was Derived (top).

Group 4 - Highly Cracked Oils.

This group represents the extreme of thermal treatment and although the processes that formed them are not intended to produce liquid products, the product slate is probably representative of what occurs in all thermal treatments to varying degrees. In Figure 13 is the feedstock used by Sundaram of Brookhaven in his novel flash pyrolysis process in methane. Note the richness of the carbohydrate peaks compared with the fir feedstock shown in Figure 11. This is evidence for the need for standard biomass samples for comparing different methods. The conversion of these primary pyrolysis products to condensed aromatics is complete and includes naphthalene (128), methyl naphthalene (142), acenaphthalene (152), fluorene (166), anthracene (178), pyrene (202), benzanthracene (228), and benz(a)pyrene (252). [Other isomers contribute to many of these masses and may be more important than the examples cited.] The simplicity of the spectrum is striking.

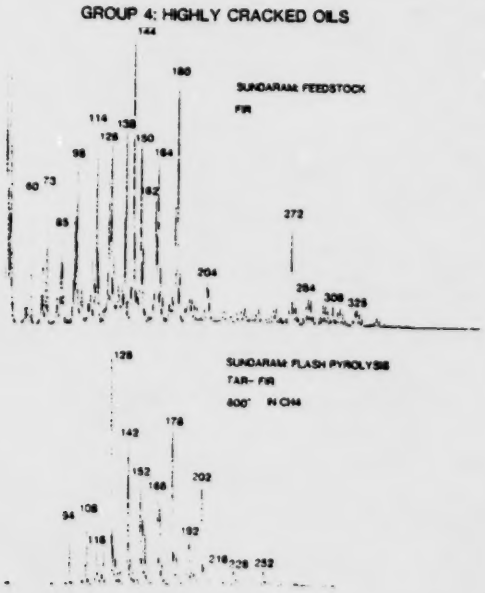

FIGURE 13. Mass Spectra of the Tar Derived from the Flash Pyrolysis of Fir in CH_4 (Sundaram) (bottom) and the Primary Pyrolysis of the Feedstock from which it was Derived (top).

Two other tars from gasification processes are shown in Figure 14. The tar from Reed's downdraft oxygen gasifier resembles Sundaram's in the sparseness of peaks, although naphthalene is missing and the higher-molecular-weight poly-nuclear aromatics are enriched. Diebold's fast pyrolysis scrubber tar is less cracked than these other two samples but is still dominated by the condensed aromatics.

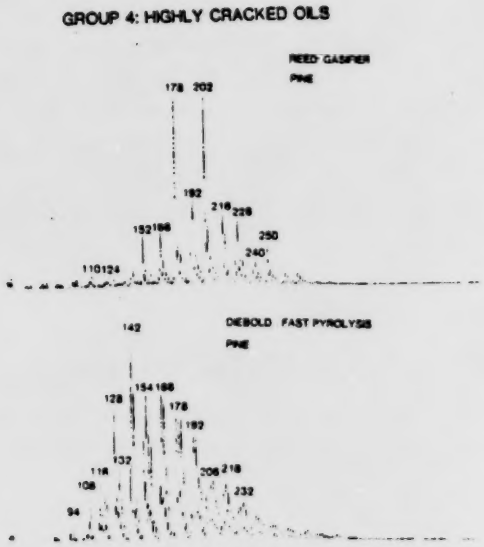

FIGURE 14. Mass Spectra of the Tar Derived from the Fast Pyrolysis of Pine (Diebold) (bottom) and the Tar Derived from the Oxigen Downdraft Gasifier (Reed) (top).

SUMMARY

The method outlined above provides a rapid and instructive "fingerprint" of the complex oils derived from biomass. The method allows various oils to be placed in one of four classes: primary oils, slightly cracked oils, condensed oils, and highly cracked oils. In addition, the relative contribution of cellulose, hemicellulose, and lignin to the pyrolysis oil can be estimated. Feedstock characterization may be of some use since significant variation among the feedstocks shown here was noted particularly in the pyrolysis of the cellulose present in whole wood samples. The technique may be of some value to researchers in optimizing the liquefaction process, by taking advantage of observations made in this oil screening process such as the effect of removing extractives on the vacuum pyrolysis of aspen. The results of this work are also of use in calibrating the mass spectrometer because of the availability of more quantitative analysis (GC/MS) for certain samples.

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ACKNOWLEDGEMENT

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LIQUID FROM BIOMASS BY PYROLYSIS
ANALYTICAL ASPECTS

H. Ménard, D. Bélanger, G. Chauvette, M. Grisé, A. Martel
Département de chimie
Université de Sherbrooke
Sherbrooke (Québec) Canada
J1K 2R1

INTRODUCTION

We analysed pyrolytic tar samples obtained from three different laboratories:

C. Roy's laboratory (Vacuum Pyrolysis) (1)

D.S. Scott's laboratory (flash pyrolysis) (2)

J.M. Pepper's laboratory (high pressure pyrolysis) (3)

We made the analysis from original samples and the concentrations are reported in weight percentage by sample weight. The tars were produced from poplar aspen (Populus Tremuloides).

Water determination

Direct quantification of water in pyrolytic tar was performed by the Karl Fischer Technique. This technique is recommended for water determination in pyroligneous mixtures rather than by the Dean Stark distillation method.

TABLE I

Vacuum pyrolysis	(1)	34.7% water
Flash pyrolysis	(2)	22.1% water
High pressure pyrolysis	(3)	11.4% water

Acid Analysis

We analysed acidic compounds by using high pressure liquid chromatography after reaction with Bromo α acetophenone (1984); this method enabled us to specifically analyse carboxylic acids.

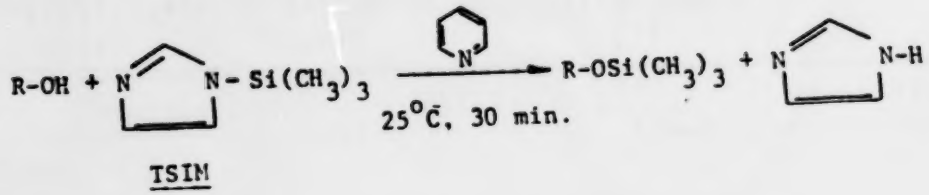
TABLE II

ACID	Vacuum Pyrolysis (1)	Flash Pyrolysis (2)	High pressure Pyrolysis (3)
Glycolic	0.052%	0.47%	0 %
Formic	3.94 %	1.37%	0.05%
Acetic	9.72 %	4.28%	0.55%
Propionic	1.02 %	0.98%	0.25%
Butyric	0.13 %	0.08%	0.03%
Pentanoic	0.78 %	0.2 %	0.11%
Hexanoic	0.20 %	0.1 %	0.09%
Heptanoic	0.0 %	0 %	0 %
Unknown	2.6 %	1.4 %	--
Total	18.91 %	9.35%	1.08%

Sugar Analysis

The analysis of monosaccharides such as levoglucosan, glucose, arabiose, etc. can be done by gas chromatography equipped with a splitter system.

In order to achieve good separation, silylation of sugars was done with N-trimethylsilyl Imidazole. The derivatives were injected on a fused quartz capillary column OV-101 of 12 meters length.



TSIM

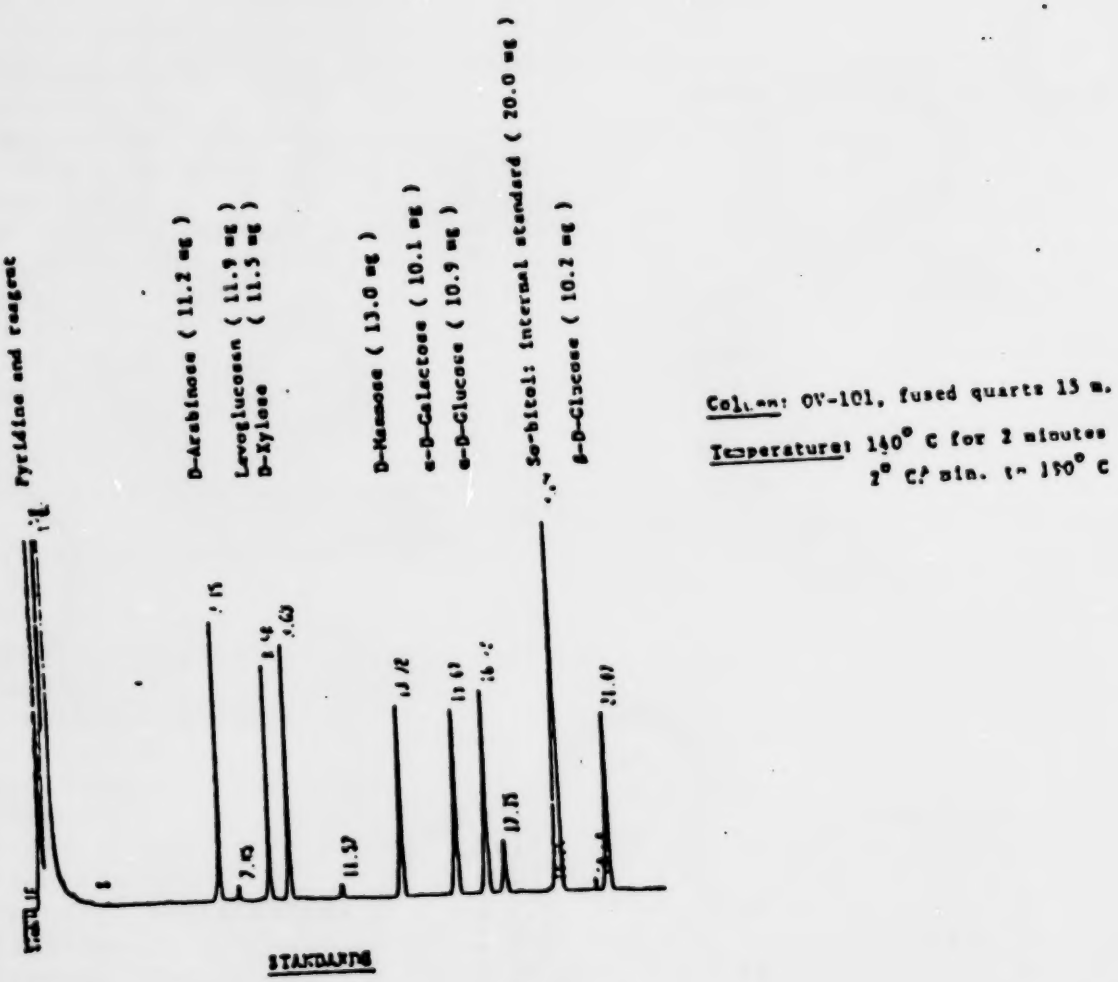


FIGURE 1. Shows a chromatogram of monosaccharide standard.

TABLE III

Sugar	Vacuum Pyrolysis (1)	Flash Pyrolysis (2)	High pressure Pyrolysis (3)
D-Arabionose	--	--	--
Levoglucosane	0.82%	1.14%	--
D-Xylose	--	--	--
D-Manose	--	--	--
D-Galactose	--	--	--
α-D-Glucose	0.02%	0.46%	--
β-D-Glucose	--	--	--
Total	0.84%	1.60%	--

Complementary analysis

The use of gas chromatography with columns having different stationary phases such as carbowax 20M and OV101 allows the analysis of the following substances.

TABLE IV

Products	Vacuum pyrolysis (1)	Flash pyrolysis (2)	High pressure pyrolysis (3)
Acetol	1.19	3.2	0.3
Anisole	0	0.04	
Cyclohexanol			
α-Angelilactone	0.02		
Furfural	0.6		0.19
Methyl-Cyclopentene-1-one	0.04	0.6	0.22
Methyl 5 furfural	0.15	0.05	0.1
Butyrolactone	0.69	0.15	0.17
Valerolactone		0.18	
Furfural Alcohol		0.48	0.1
Methyl Cyclo Pentenolone		0.2	0.08
Guaiacol	0.22	0.25	0.52
Dimethyl-2 6-phenol	0.04	0.37	0.06
3-hydroxy-2-methyl-4-pyrone		0.27	0.04
Phenol	0.38	0.41	0.62
Trimethyl-2-4-6-phenol		0.02	
Cresols		0.21	0.18
Ethyl-2-phenol		1.28	0.47
Dimethyl-2.3-phenol	0.25	0.98	0.11
Eugenol		0.2	0.19
Dimethyl-2.5-phenol		0.12	0.03
Syringol		0.39	1.4
Iso Eugenol		0.07	0.35
Catechol		0.51	0.36
Hydroquinone	0.14	0.09	
Resorcinol	0.09	0.31	0.49
Methanol Acetaldehyde	2.17	1.14	0.08
Butanone-2	0.85	0.36	0.045
Syringol dehyde	0.23	0.69	
TOTAL	7.06	12.57	6.06

The summation of all organic compounds and water is listed in Table V. We observe that the tars are not completely identified. and according to vacuum distillation we concluded that pyrolysis does not lead entirely to monomers. In fact we probably obtain partial thermal degradation of lignin and cellulose due to incomplete pyrolysis.

TABLE V

		identified portion of the tar
Vacuum pyrolysis	(1)	61.5 %
Flash pyrolysis	(2)	45.62%
High pressure pyrolysis	(3)	18.54%

ACKNOWLEDGMENT

We thank Dr. E. Chornet for the access to the Karl Fisher Instrumentation. The authors gratefully acknowledge financial support from the Canadian Forestry Service, Department of Environment (ENFOR Programme).

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CHARACTERIZATION OF PYROLYTIC OILS PRODUCED BY DENSE GAS EXTRACTION

BY

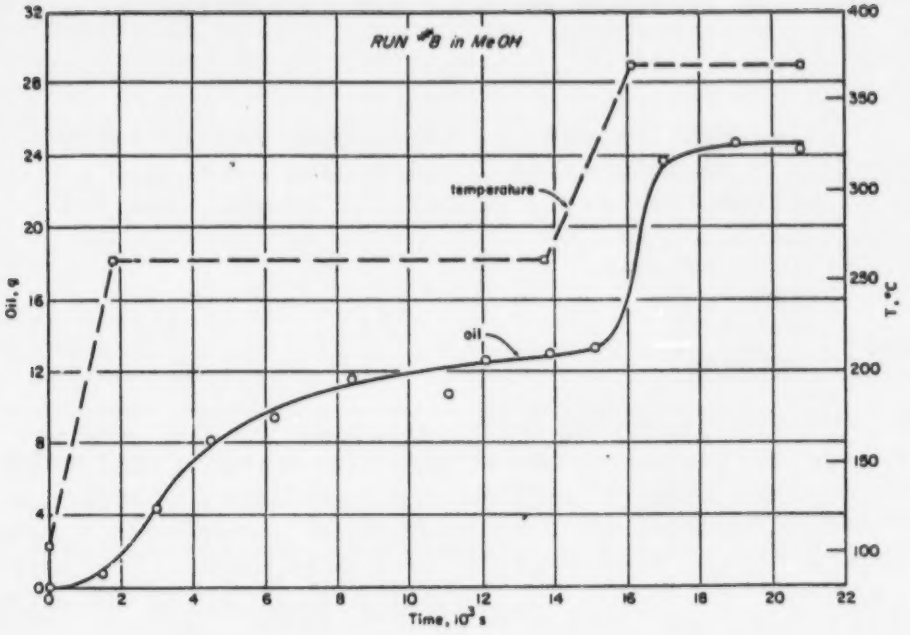
J.L. GRANDMAISON, S. KALIAGUINE AND A. AHMED
Department of Chemical Engineering
Université Laval, Québec, QC Canada, G1K 7P4

INTRODUCTION

DGE with methanol

The pyrolytic oils examined in the present paper have been collected by dense gas extraction (DGE) from aspen wood (Populus tremuloïdes) in our laboratory (Labrecque et al, 1982 & 1983). Methanol was used as solvent in most of the cases but in some runs THF was also used. The details of the process is described in another paper in this meeting (Kaliaguine et al). Here, some results on the characterization of these oils are presented.

The cumulative production of oils versus time and temperature program is shown in Figure 1 for run # 8, in which DGE has been performed in methanol. From this curve, two oils may be defined: oil # 1 and oil # 2, obtained below and above 250°C respectively. Two temperature plateaus at 250 and 350°C are maintained until the oil yield reaches a steady value. The liquid fractions are evaporated under dynamic vacuum at 75°C and oil fractions are collected.



Pressure: 10.20 MPa
flow rate: 0.212 g/s.

FIGURE 1. Typical DGE in MeOH.

Some properties of oil # 1 and oil # 2 are shown in Table 1 to emphasize the differences. These are as follows:

1) Oil # 1 is more viscous, possibly because of larger fragments from a less efficient pyrolysis of wood, which would also explain why oil # 1 is less soluble in usual solvents;
2) water content is relatively low, which means the evaporation is successful in this regard;
3) oil # 2 is more oxygenated (% O and H/C value).

Table 1. Some Properties of Oils # 8-1 and # 8-2

	Oil no 1	Oil no 2
Appearance:	Dark Brown Viscous	Dark Brown Fluid
Solubility in:		
Pentane:	Slightly	Slightly
Ethyl Ether:	Partly	Nearly Sol.
Methanol:	Nearly Sol.	Nearly Sol.
T.H.F.:	Sol.	Sol.
% Water:	< 0.50	< 0.50
Elementary analysis:		
% C:	60.25	55.42
% H:	9.17	7.21
% O:	29.98	36.77
% N:	0.60	0.60
H/C:	1.826	1.561
O/C:	0.373	0.497

Characterization of oils from DGE with methanol

The chromatograms on Carbowax - 20M of both oils are complex and have distinct patterns (Figure 2), systematically obtained with all the oils from DGE in methanol. The chromatogram of oil # 1 exhibits more important peaks in the long retention times than the one of oil #2.

The use of extraction with bases can help in the characterization approach (Elder and Soltes (1980) Kallury and Tidwell, 1982). Using this method, three fractions were obtained with each of the two oils: 1) strong acids; 2) weak acids and 3) neutral compounds (Figure 3). Attempts to

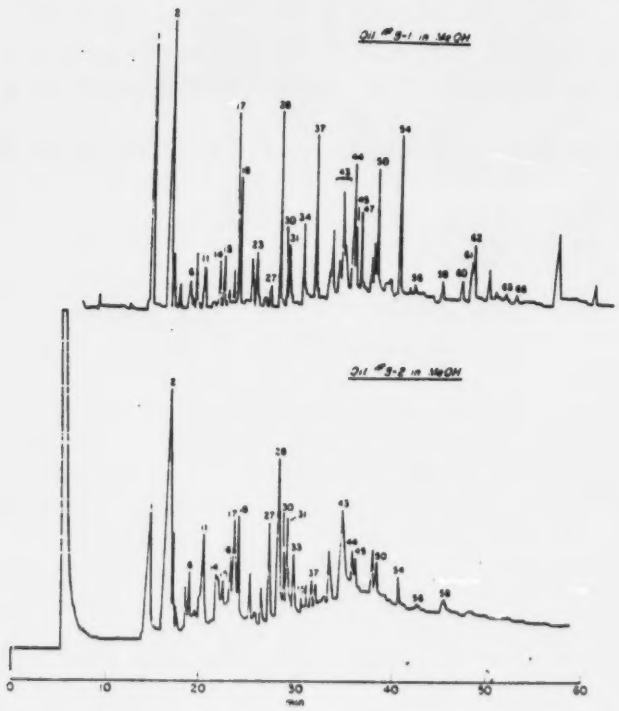


FIGURE 2. Chromatograms of oils #8-1 and #8-2 (on Carbowax # 20M)

PYROLYTIC OIL # 8

ethyl ether

		Oil # 8-1	Oil # 8-2
filtration →	residue		
$NaHCO_3$ →	strong acids	1.6%	1.5%
NaOH →	weak acids		
	soln in ether	20.6%	12.5%
	insoln in ether	9.3%	0%
HCl →	basic compounds	3%	0%
→	neutral compounds	4.2%	16.3%
	Total recovery	38.3%	30.3%

FIGURE 3. Isolation of Acidic and Neutral Fractions.

isolate basic compounds resulted in practically negligible (< 0.1%) extraction with a 5% solution of HCl. The total recovery is relatively low, between 30 to 36% of oils was isolated because the amount of hydro-soluble substances is large. Important differences can indeed be seen by comparing the chromatograms of the six extracted fractions (Figure 4) with those of the two original oils (Figure 2).

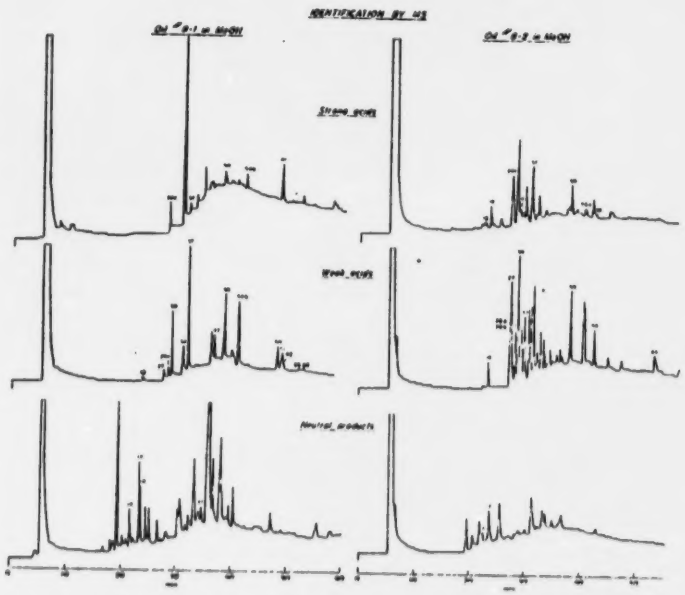


FIGURE 4. Chromatograms of Extracted fractions with GC/MS identifications. (on Carbowax - 20M)

During extraction of weak acids of oil # 8-1, an important portion (9.9%) became insoluble in ethyl ether. Probably, some weak acids repolymerize in the presence of sodium hydroxide; this portion is however soluble in THF.

The GC/MS technique is in widespread use (Elder and Soltes 1980 and Molton et al 1981), for the identification of the products of biomass pyrolysis. In our case*, it allowed us to identify twenty-seven compounds so far (Table 2). Some structures have been confirmed by comparing their mass spectra with those of standards (highly probable); by comparing with literature spectra (probable); the identifications performed by us on the basis of the fragmentation study have been designated as tentative.

* The MS spectra were recorded in the laboratory of Prof. Michel Bertrand, Chemistry Department, Université de Montréal. The MS was a VG 12-12 quadrupole.

Table 2. Compounds in Pyrolytic Oil # 8 (Identified by MS)

	OIL # 8-1	OIL # 8-2
KETONES (CYCLO ?):		
27 KETONE C-8 (PM. 126)	T	T
28a KETONE C-7 (PM. 112)	T	T
28b KETONE C-8 (PM. 126)	-	T
ACIDS:		
2 ACETIC ACID	P	-
14 BUTYRIC ACID	P	-
28c HEXANOIC ACID	P	-
FURANS:		
14 FURAN ET-2, ME-5	T	-
15 FURAN AC-2 OME-5	-	T
18 FURFURYL ALCOHOL	T	T
AROMATICS MONO-HYDROXY:		
37 PHENOL	H	H
43 BENZOATE METHYL, OME-4	T	-
AROMATICS DI-HYDROXY:		
30 GUAIACOL	H	H
33 GUAIACOL ME-6	-	T
34 GUAIACOL ME-5	P	-
44 EUGENOL	-	H
47 GUAIACOL VINYL-5	T	-
54b isoEUGENOL	P	-
56 BENZOATE ME, OME-3, OH-4	-	T
61 VANILLIN	H	-
62 GUAIACOL (PROPANONE-2)-5	T	-
66 GUAIACOL ACETYL-5	T	-
AROMATICS TRI-HYDROXY:		
50 PHENOL diOME-2,6	H	H
54a PHENOL diOME-2,6, ME-4	-	T
56 PHENOL diOME-2,6, ET-4	-	T
60 PHENOL diOME-2,6, ALLYL-4	T	-
65 PHENOL diOME-2,6, isoALLYL-4	T	T
OTHERS AROMATICS:		
17 BENZOATE METHYL	T	T

H = highly probable; P = probable; T = tentative.

The identified compounds may be grouped in the following classes:

1) furans
2) phenols
3) guaiacols
4) dimethoxy - 2,6 phenols
5) aliphatic ketones
6) carboxylic acids

In future runs with GC/MS, we expect to obtain more information by using derivatization reactions (Drozd, 1981).

Table 3 is a list of 10 additional compounds which were further identified by comparing GC retention times with those of standards. These identifications need to be confirmed by other analytical techniques. Most of these compounds are very soluble in water, which explains why they were not detected by the GC/MS analysis performed on the extracted fractions.

Table 3. Compounds in Pyrolytic Oil #8 (Identified by GC only) (To be Confirmed)

		Oil # 8-1	Oil # 8-2
ACIDS:			
1	FORMIC ACID	+	+
11	PROPIONIC ACID	+	+
23	VALERIC ACID	+	-
35	HEPTANOIC ACID	-	+
FURANS:			
6	FURFURAL	+	+
AROMATICS MONO-HYDROXY:			
43	PHENOL +eoPR-2		
AROMATICS DI-HYDROXY:		+	+
42	BENZALDEHYDE OH-2, OME-3	+	+
45	BENZALDEHYDE di OME-2,3	+	+
58	BENZALDEHYDE di OME-2,4	+	+
OTHERS AROMATICS:			
31	BENZYLIC ALCOHOL	+	+

At that point of the identification work it was felt that although the extraction technique had been of some use in the characterization of a rather large number of compounds in the oils, this technique was of limited application since many compounds are not recovered. Therefore the HPLC technique was retained for further work.

Pyrolysis of wood components versus temperature

Soltes (1981) claims that the thermal decomposition of wood does not progress at an even pace, but rather in a step-wise manner, with the hemicelluloses breaking down first at temperatures of 200 to 260°C. Cellulose follows in the temperature range 240-350°C, with lignin being the last component to pyrolyze at temperatures of 280 to 500°C.

Considering the results obtained in our laboratory, this scheme needs to be modified. For example, in experiment # 8, at the end of the first plateau (250°C), the oil yield (oil # 8-1) represents 32% of the original wood, while wood contains around 25% hemicelluloses (Goldstein, 1980). Also, phenols coming from lignin (peaks 30, 33, 34, 44, 47, 50, 54a, 54b, on Figure 2) are positively identified in oil # 1. Therefore a superficial analysis of our results shows that lignin is already significantly pyrolyzed at temperatures not higher than 250°C.

In experiment # 34 eight oil fractions were collected instead of two (see conditions, Table 4). The purpose was to follow the evolution of products with temperature, specially those coming undoubtedly from each of the three wood constituents. Fraction # 34-1 is partly soluble in THF and is composed surely of partially pyrolyzed fragments of wood constituents. Fractions # 34-2 to 34-8 become gradually more fluid as the temperature of extraction is elevated (indicating an increased efficiency of the pyrolysis process).

Table 4. Run #34 (DGE with MeOH)

FRACTION NO.	TEMPERATURES	OIL G	
1	120-190	1.0	
2	190-235	2.0	
3	235-245	1.2	OIL NO.1
4	245-275	0.3	
5	275-330	3.7	
6	330-350	5.2	
7	350	1.6	OIL NO.2
8	350	0.4	

Empirically, the chromatograms (Figure 5) begin to have a complex nature above 190°C. Peaks 1 to 34 are predominating above 275°C. They are also present at lower temperatures, but they are probably coming mainly from cellulose degradation.

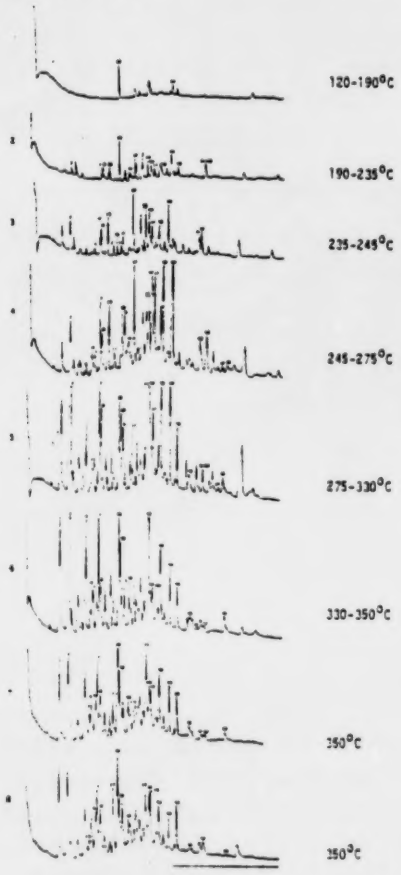


FIGURE 5. Chromatograms of Oils # 34 (on Carbowax - 20M)

On the other hand, products originating from lignin (peaks N° 37 and 50 to 66) are relatively abundant in fractions # 34-1 to 34-5 (temperatures 190-330°C) while they continue to appear until fraction # 34-8 (350°C). The observed breaking down of lignin at temperatures 120-190°C is in agreement with the partial delignification described by Hansen and April (1982) in a series of alcohols at temperatures 175 and 205°C. Also, the fact that the pyrolysis of lignin continues on up to 350°C, after a stop corresponding to the plateau at 250°C means that lignin, apparently, is cracking in two steps; the second coming from lignin, either unconverted or as recondensed fragments.

Table 5 gives, for the six most abundant fractions of experiment # 34, the mass percentage of the extracts collected by HPLC following the sequence of solvents suggested by Ménard et al (1982). The main features of these results is the high percentage of extraction in THF and the low proportion of the methanol extract.

Table 5. Mass percentage of HPLC extracts in the fractions collected in experiment # 34

Oil fraction / Solvent	34-1	34-2	34-3	34-5	34-6	34-7
hexane	1.2	1.1	2.3	0.0	1.8	2.7
THF	79.8	87.0	85.7	96.3	95.7	84.3
Methanol	8.1	7.5	4.8	0.4	0.6	4.5
Water	2.7	1.1	2.9	0.0	0.4	2.9
50% Water 50% AcOH	8.2	3.3	4.3	3.3	1.5	5.6

preliminary study of oils from DGE with THF

Some experiments of dense gas extraction were made using THF rather than methanol as solvent. The cumulative oil yield curve obtained (run # 112, see ref. 3) was noticeably different from that with methanol. The oil yield remains low below 250°C but increases rapidly with temperature above 250°C.

The chromatogram of oil # 1 obtained from DGE in THF has a pattern similar to the one of oil # 1 collected from methanol, except for some new large peaks (indicated with arrows on Figure 6). Moreover, the chromatogram of oil # 2 is different from the one obtained for the corresponding oil with methanol; it contains some of the large peaks previously mentioned and also relatively high concentrations of products coming from lignin pyrolysis (peaks N° 50 to 66 on Figure 6).

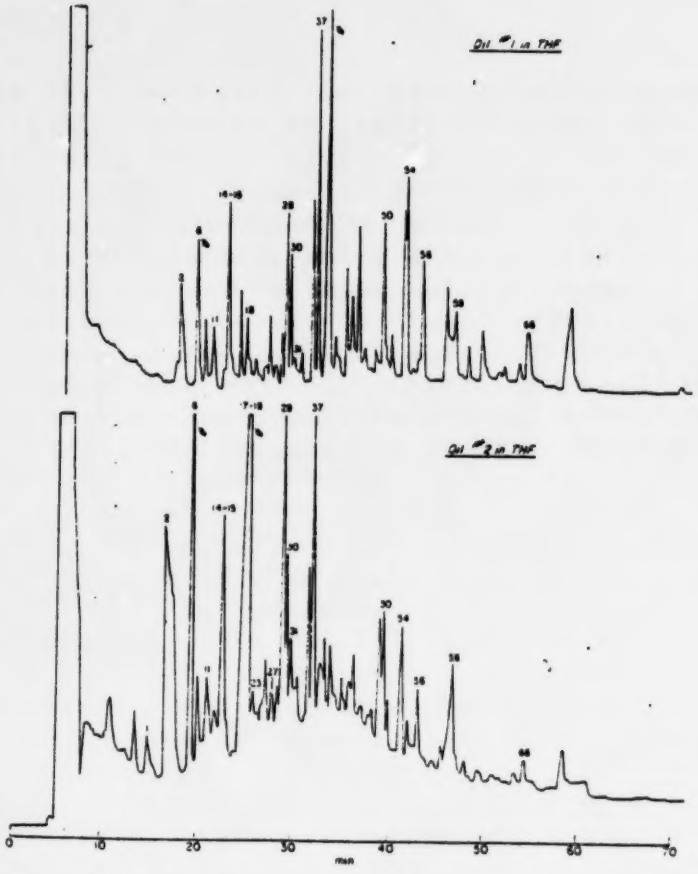


FIGURE 6. Chromatograms of oils # 112-1 and # 112-2

The lower yield in oil # 1 observed in THF compared to methanol (Kaliaguine et al) has to be linked to this extraction of lignin fragments at higher temperatures. Therefore the ligneous material not recovered in oil # 1 is retained in the char either as intact or recondensed fragments.

As to the large new peaks observed in oil # 1 and oil - 2 from THF (peaks 6, 14, 15 and 18), they have been tentatively described to furan compounds (furfural, furan ethyl methyl, furan acetyl methoxy and fufuryl alcohol respectively). It seems therefore that THF is not an inert solvent and reacts in DGE conditions.

CONCLUSION

This paper should be considered as a presentation of the present status of an ongoing program on the characterization of pyrolytic oils. At this time, 37 compounds have been identified by use of GC and GC/MS. The systematic GC and GPC analysis of fractions produced by HPLC should permit the study of the large molecular size compounds which may not be detected by GC alone. The analysis of oils, obtained so far by DGE, shows that lignin is breaking down in 2 stages. The first stage happens at temperatures not exceeding 250°C, simultaneously with the pyrolysis of hemicelluloses. The second one between 250 and 350°C is simultaneous with the thermal degradation of cellulose.

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Section 6

CATALYSIS APPLIED TO UPGRADING

HIGH-TEMPERATURE CATALYTIC HYDROGENOLYSIS AND ALKYLATION OF ANISOLE AND PHENOL

R.K.M.R. KALLURY AND T.T. TIDWELL
DEPARTMENT OF CHEMISTRY, UNIVERSITY OF TORONTO
TORONTO, ONTARIO, CANADA M5S 1A1

D.G.B. BOOCOCK AND D.H.L. CHOW
DEPARTMENT OF CHEMICAL ENGINEERING, UNIVERSITY OF TORONTO
TORONTO, ONTARIO, CANADA M5S 1A1

INTRODUCTION

For several years we have been engaged in the analysis of the chemical composition of the oils derived from the catalytic hydrogenation of aspen wood. The purpose of this research is to gain an understanding of the general types of compounds present, and also how the yields of the different products change with reaction conditions. Using this knowledge, we hope to both understand some of the chemical processes which occur during wood liquefaction, and also to learn how to upgrade the final product to a more desirable constitution. The first report on our separation scheme and analytical procedures has appeared (Boocock, D.G.B., et al, 1983). The current report deals with experiments on the reaction of model compounds under the reaction conditions.

RESULTS

Reactions were carried out using the procedure described for wood liquefaction by Raney nickel (Boocock, D.G.B., et al, 1980). The "BASF catalyst" was composed of Al_2O_3 with 15% MoO_3 and 3% NiO. Product analyses were carried out using GC, ^{1}H-NMR, and GC-MS techniques, and whenever possible products were isolated by preparative gas chromatography and their identities confirmed by ^{1}H-NMR. The results are summarized in Tables 1-3.

DISCUSSION

Hydrogenation of phenol with the BASF catalyst yields predominantly benzene, with lesser amounts of

cyclohexane and methylcyclopentane (Table 1). Since cyclohexane does not give methylcyclopentane this latter product evidently arises from a cyclohexanol intermediate formed in the reaction, which does not however survive (equation 1). The benzene is evidently derived from hydrogenolysis of phenol (equation 2). Cyclohexanol was found in a separate experiment to yield cyclohexane, presumably through the cyclohexyl cation but possibly by direct hydrogenolysis (equation 3). The reaction of benzene under these conditions has not yet been studied so it cannot be specified if part of the cyclohexane formed arises directly from benzene. Reaction of the cyclohexyl cation with phenol would lead to the observed cyclohexylphenol, cyclohexylbenzene, and biphenyl (equation 4).

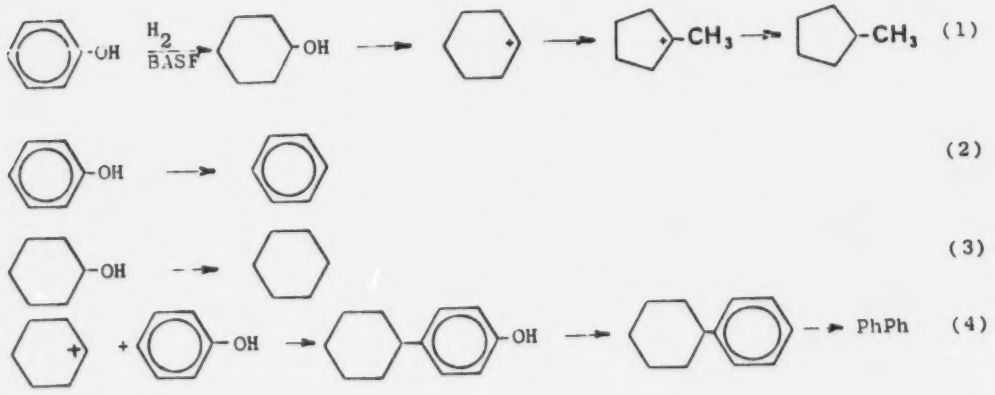


Table 1. Hydrogenation with BASF catalyst, 450°C, 400 psi initial H_2 pressure

Substrate	% conversion	methyl-cyclopentane	cyclo-hexane	cyclo-hexene	benzene	toluene	Me_2-benzene	Me_3-benzene	Me_4-benzene	Me_5-benzene	Other
cyclohexane	2		98		2						
cyclohexene	100		85		15						
cyclohexanol	100	20	65		0.3	0.1	0.1				
cyclohexanone	100	3	40	36	0.5	0.1	0.1				b
phenol	100	7	16		60	2	2	2	2		c
anisole	98	2	5		20	18	12	15	5		d
phenol/MeOH[a]	90	1	2	1	7	7	8	16	20	10	e
anisole/MeOH[a]	96	0.5	1		2	5	5	13	16	8	f

[a] 1/1 (by wt.) [b] cyclohexylbenzene (7), biphenyl (4), phenol (4), [c] cyclohexyl benzene (2), biphenyl (3), cyclohexylcyclohexane (2). [d] phenol (10), mono- and dimethylphenol (10)

[e] methylphenols (3), dimethylphenols (13), trimethylphenols (5), hexamethylbenzene (2).

[f] phenol (5), dimethylphenols (14), trimethylphenols (4), tetramethylphenols (4).

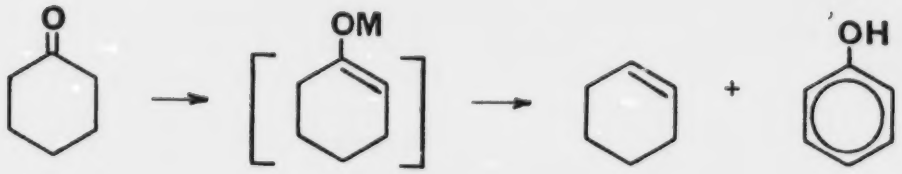
There is precedent for these steps in the literature, (Rylander, 1979, and Mihalovic et al 1971) including early reports of phenol reduction with ammonium molybdate/charcoal (Cawley, 1932) and molybdenum sulfide (Moldawski, and Lifshitz, 1933). This area has been reviewed, (Shuikin, and Erivanskaya, 1960) and in a recent report (Bagnall, and Jeffery, 1981) on phenol reduction with platinum black it was found that if the product benzene was removed with N_2 gas that further reduction of benzene to cyclohexane could be supressed and the yield of benzene maximized.

The formation of Methylcyclopentane in the reduction clearly indicates a cationic intermediate; this rearrangement has been previously observed (Illes, V., and Schindlbaner, 1974) on the reaction of cyclohexene with Al_2O_3/SiO_2 catalyst at 300°C. The rearrangement of the cyclohexyl cation to the 1-methylcyclopentyl cation in solution is well known, (Arnett, and Petro, 1978) but the cyclohexyl radical does not rearrange to the 1-methylcyclopentyl system (Beckwith, and Ingold, Vol. 1, 1980).

The reaction of cyclohexanone does not give cyclohexanol as a major intermediate, as the products from reduction of cyclohexanone and cyclohexanol are different, especially the significant amount of cyclohexene formed from cyclohexanone. A small contribution of this path cannot however be excluded. Possibly cyclohexanone leads to a metal enolate (equation 5) which is converted to both phenol and cyclohexene. Formation of such an enolate has been proposed (Manninger, et al, 1977) as a intermediate in the conversion of cyclohexanone to phenol by Pt catalysts.

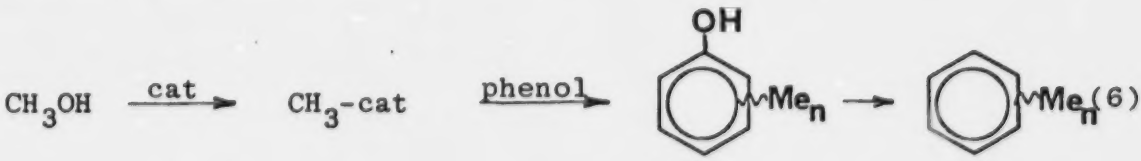
The results in Table 2 show that the maximum conversion of phenol to benzene is achieved at lower H_2 pressures (400 psi) at 450°C. The formation of methylbenzenes in one run (Table 2) is hard to explain, and this result should be viewed with suspicion until it is confirmed.

Table 2. Reaction Variables in the BASF catalyst hydrogenation of phenol[a]



(5)

Reaction of phenol in the presence of methanol leads to the formation of large quantities of methylbenzenes (Table 1). Evidently an active electrophilic alkylating agent is formed by interaction of the catalyst with methanol, and this agent reacts most likely by alkylation of phenol. Deoxygenation of the methylated phenols then gives the methylbenzenes (equation 6).



(6)

Such alkylation of phenols has been observed previously (Boocock, et al, 1983).

The reaction of anisole gives a similar product distribution to the reaction of phenol in the presence of methanol (Table 1) and it is likely that anisole reacts initially to give phenol and a methylating agent complexed to the catalyst. It is probable that free methanol is not formed, as in another experiment it was shown that methanol and the catalyst liberated CH_4, whereas none was observed from anisole.

The reaction of anisole with other catalysts (Table 3) shows a deleterious effect of added water on anisole conversion, and a greater activity of Raney nickel in the absence of methanol for conversion of the anisole compared to the other catalysts. The nickel catalysts also give much greater yields of ring saturation (cyclohexane, cyclohexanol, and cyclohexyl methyl ether) than does the BASF catalyst, which gives predominantly aromatic hydrocarbons from either phenol or anisole.

Table 3. Effect of Catalyst Variation on Hydrogenation Anisole (1000 psi)

Catalyst	T(°C)	anisole	cyclohexyl methyl ether	cyclohexane	cyclohexanol	phenol	cyclo-hexanone	benzene	phenyl-cyclohexene	Other
Ni/Al (H_2O)	350	45	25	5	14	1				
Ni/Al	350	26		26	3	18	10	2		
Ni/Al (H_2O)	250	32	4		4	3	2			
Ni/Al	250	68	10	2	2	2	5			
$NiCO_3$ (H_2O)	350	72			7	3	4		2	
$NiCO_3$	350	16		46	10					
$NiCO_3$ (H_2O)	250	98				2				
$NiCO_3$	250	15	45	26	15					
Raney Ni	250	5		49		8		16	5	[a]
Raney Ni(MeOH)	250	28	10	8	24	2	2	5		[b]

[a] methylcyclopentane (7)

[b] methylphenols (16)

ACKNOWLEDGEMENT

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FEASIBILITY OF THE PRODUCTION OF HYDROCARBONS FROM ASPEN POPLAR PYROLYTIC OILS OVER H-ZSM5

BY

P. CHANTAL, S. KALIAGUINE, J.L. GRANDMAISON, A. MAHAY
DEPARTMENT OF CHEMICAL ENGINEERING
UNIVERSITÉ LAVAL, QUÉBEC, QC, CANADA G1K 7P4

INTRODUCTION

In previous reports (Kaliaguine, 1981, 1982) two possible routes for the heterogenously catalyzed upgrading of pyrolytic oils from biomass to produce hydrocarbon mixtures have been suggested.

The first one involves dehydration and decarboxylation over the hydrogen form of pentasil zeolites and the second one deals with hydrotreatment of the oil (with H_2 or H_2 + CO) over a supported oxide catalyst.

In the present paper we will report a study of the first kind of process in which the oil is vaporized in a flow of inert gas and contacted with H-ZSM5.

The oil under study was produced by dense gas extraction in methanol, and in order to provide a uniform feed in all experiments we have utilized a blending of the so-called oils N^0 2 from eight experiments. The C, H, O, N analysis of this blending is shown in Table 1 along with the corresponding analysis of methanol for comparison. The water content of this oil was less than 0.5 mass %.

Table 1. C, H, O, N, analysis

- Mass percentage

	Methanol	Oil # 2
C	37.5	55.1
H	12.5	7.2
O	50.0	37.2
N	0	0.5

- Atomic ratio

H/C	4.00	1.57
O/C	1.00	0.51

EXPERIMENTAL SET-UP

A schematic diagram of the experimental set-up is shown on Figure 1. Oil is injected in a flow of helium using a piston pump (Sage 220) and fed to a microcatalytic fixed bed reactor loaded with 1.0± 0.05 g of undiluted H-ZSM5. We prepared this catalyst with a Si/Al value of 22 and a Al/Na value before cationic exchange of 1.1. This sodium is totally exchanged during the activation procedure in the H form, since the sodium was below the limit of detection of the PIXE/PIGE analytical technique (Szöghy, E., et al). The size distribution for this zeolite was bimodal with maxima in the 1-2 and 15-20 µm. Scanning electron microphotographs show total absence of amorphous material and X-Ray diffraction patterns show the absence of other cristalline phases in any significant amount.

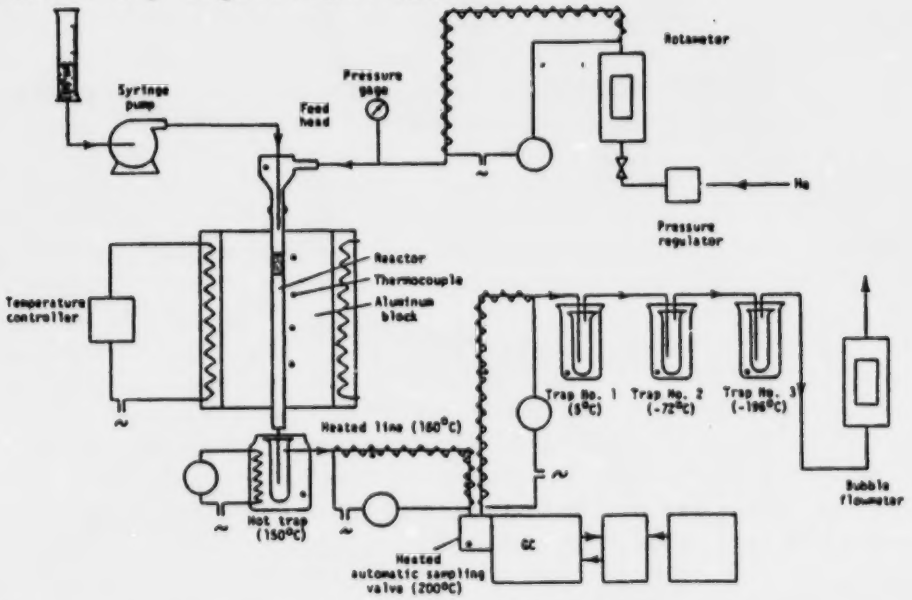

FIGURE 1: Experimental set-up

The gases leaving the reactor pass through a hot trap at 150°C in which heavy fractions of the unconverted oil are collected. The vapor fraction is then introduced into an automatic sampling valve maintained at 200°C. After the valve this vapour is condensed as three fractions collected at 5, -72 and -196°C respectively.

The tube reactor can be dismounted from this set-up and installed on a regeneration apparatus. This system allows the regeneration of the catalyst after a run by burning the coke at 500°C in pure air, and the collection and measurement of the H_2O and CO_2 formed during this combustion by adsorption on Drierite™ and Ascarite™ respectively. A quantitative determination of the coke formed is thus made for each run. All results reported thereafter were obtained with catalysts having been regenerated at least once.

The experimental conditions are reported in Table 4. Experiments were performed at temperatures from 350 to 450°C with LHSV comprised between 0.5 and 2.5 h^{-1}. The oil was fed either pure or mixed with five or ten mass percent of methanol. The nominal flow rate of helium was 6 cm^3/ min. In all experiments oil was fed to the reactor for 3600 s except for the runs at higher oil flow rates (LHSV > 2. h^{-1}) where that time was 2900 s.

EXPERIMENTAL RESULTS

Figure 2 shows two chromatograms for the oil fed and the tar collected in the hot trap during experiment No 3. These were recorded using a 50 m. capilary column WCOT carbowax 20 M and a FID detector in a Perkin-Elmer Sigma 3 gas chromatograph.

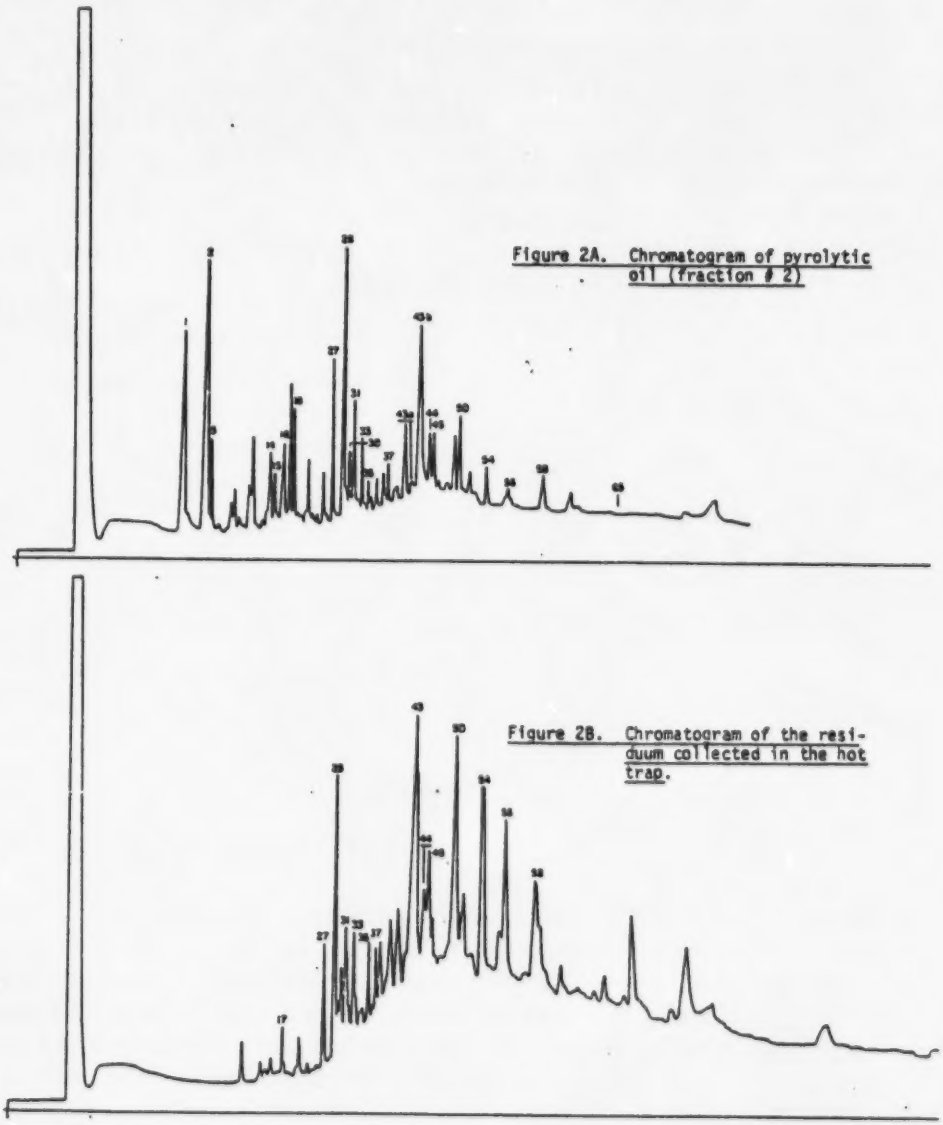

Figure 2A. Chromatogram of pyrolytic oil (fraction # 2)

Figure 2B. Chromatogram of the residuum collected in the hot trap.

FIGURE 2. Comparison of the chromatograms of the pyrolytic oil and the residuum.

This kind of comparison allow the classification of the identified products as shown on Table 2. Some of the products in the oil are not found in the tar, some have diminished in concentration whereas some have increased. It is interesting to note that among the products of this last category, the one with the lowest retention time is dimethoxy2,6 phenol which among the phenols is the smallest to be unable to penetrate into the pores of the ZSM5 lattice.

Table 2: Products identification for Figure 2

Not present in the tar	PEAK NO 1	Formic acid (Cyclopentanol)
	2	Acetic acid
	5	Cyclohexanol
	14	Butyric acid
	15	Acetyl-2 methoxy-5 furan
	16	Methoxy-4 furoïc acid
	18	Furfuryl alcohol
Partially eliminated from the tar	PEAK NO 17	Methyl benzoate
	27	C-8 ketone
	28	C-7 ketone
	30	Guaïacol
	31	Benzylic alcohol
	33	Methyl-6 guaïacol
	37	Phenol
	43	Isopropyl-2 phenol
	44	Eugenol
	45	Dimethoxy-2,3 benzaldehyde
Concentration in the tar higher than in initial oil	PEAK NO 50	Dimethoxy-2,6 phenol
	54	Isoeugenol (dimethoxy-2,6 methyl-4 phenol)
	56	Hydroxy-4 methoxy-3 methyl benzoate (dimethoxy-2,6 ethyl-4 phenol)
	58	Dimethoxy-2,4 benzaldehyde

Figure 3 shows a series of three chromatograms of the vapor fractions obtained during experiments No 1, 3 and 2 (respectively chromatograms A, B and C). The numbers

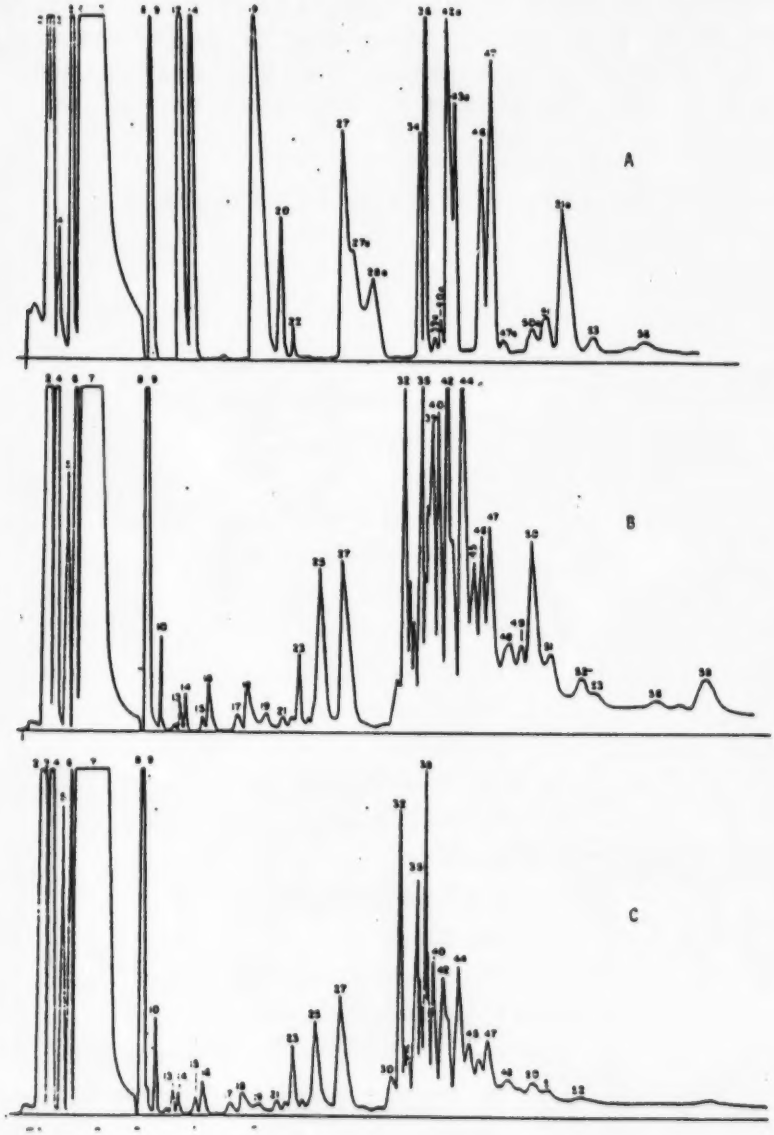

FIGURE 3. Comparison of the chromatograms of the gas leaving the hot trap obtained with pure methanol (A), 10% methanol in the oil (B), pure oil (C).

identifying the peak are reported in Table 3. Experiment No 1 is a blank conducted with pure methanol as the feed, and the product distribution in chromatogram A is very similar to the product distribution in the methanol to gasoline process in similar conditions (Chang, 1983).

Table 3: Products identification for Figure 3

Peak Number	Identification	Peak Number	Identification
2	Carbon monoxide	36	Toluene
3	Methane	39a	Dimethylhexane
4	Carbon dioxide	40	Hexanol/Cyclohexanol
5	Ethylene	40a	Octane
6	Ethane	42	Phenol
7	Water	42a	Xylenes
8	Propylene	43	2,2,5 Trimethylhexane
9	Propane	43a	Xylenes
13	Iso-Butane	44	1-Heptanol
14	Butane	45	1-Nonene
19	Pentane	46	(p.m.)-Ethyl Toluene
20	1-Pentene	47	O-Ethyltoluene
22	Cyclopentane	47a	1-Decene
27	Benzene	48	2,6-Dimethylphenol
27a	Methylpentane	50	3 ,5-Dimethylphenol
28	Hexane/1-Hexene	50a	Diethylbenzene
32	Pentanol	51a	1,2,3,5-Tetramethylbenzene
33	2,4-Dimethyl Pentane	52	1,2,4,6-Tetramethylbenzene
34	Cyclopentanol/Heptane	53	1,2,3,4-Tetramethylbenzene
35	3-Methyl Hexane		

These analysis are quantitatively reported in Table 4 under the heading "mass % in products collected in traps 1, 2 and 3". The columns C_2, C_3 and C_4 correspond to alkanes and olefins simultaneously. The column hydr. C_5-C_{10} corresponds to alkanes, aromatics and a very small contribution from higher olefins. No hydrocarbon of more than 10 carbons was produced. The column "oxyg." corresponds to all oxygenates with all unidentified products being considered as oxygenates and affected with a response factor of 0.7 in these calculations.

Table 4. Experimental Results and Conditions

Expt. N°	Temperature °C	LHSV h^{-1}	Mass % meth. in feed	Coke Mass %	Tar (150°-) Mass %	Mass % in products in traps, 1, 2 and 3.									C_5-C_{10}	Y
						CO	CO_2	H_2O	CH_4	C_2	C_3	C_4	Hydr. C_5-C_{10}	Oxyg.	%	-
1	350	1.1	100	2.0	0	0.2	0	47.3	0.5	0.7	8.0	12.1	31.3	0	30.7	0.00
17	350	0.53	0	24.0	38.0	2.0	2.1	25.0	0	0.4	17.6	0.6	13.0	39.2	4.9	0.12
19	350	0.52	10	26.9	26.8	1.4	1.6	18.8	0	0.4	16.0	0.6	19.0	42.1	8.8	0.11
8	400	0.51	0	23.8	26.2	5.8	3.9	22.5	0.1	1.4	15.3	2.2	12.6	36.3	6.4	0.30
10	400	0.50	5	19.5	23.9	5.6	2.2	34.2	0	1.5	13.2	2.7	12.2	28.4	6.9	0.15
9	400	0.49	10	14.6	14.5	7.5	2.0	16.5	0	2.0	12.3	4.8	9.0	45.9	6.4	0.39
20	450	0.52	0	22.5	22.4	8.3	2.5	12.5	0	1.6	12.3	4.2	27.3	31.3	15.0	0.59
18	450	0.49	10	21.7	10.9	6.2	1.8	25.4	0	1.2	6.6	4.7	24.8	29.3	16.8	0.21
16	300	1.3	0	22.6	46.5	0.5	1.6	9.9	0.7	0.1	14.6	0.2	24.4	48.2	7.6	0.16
11	350	1.2	0	15.2	47.7	2.1	3.4	30.0	0	0.2	29.1	0.3	10.7	31.3	4.0	0.13
13	350	1.1	5	14.8	49.2	1.2	1.7	23.6	0	0.2	20.6	0.3	14.0	38.4	5.0	0.09
14	350	1.2	10	11.5	47.7	1.9	3.5	31.4	0	0.3	0.4	0.4	19.1	43.0	7.8	0.13
2	400	1.3	0	6.0	42.7	1.4	1.8	22.6	0.5	0.4	15.2	0.4	15.9	41.8	8.2	0.10
4	400	1.1	5	13.0	45.2	1.6	1.8	14.8	0	0.4	19.7	0.5	23.6	37.6	9.9	0.16
3	400	1.2	10	13.9	30.4	1.0	1.1	5.8	0	0.2	14.3	0.4	21.2	55.9	11.8	0.26
5	450	1.2	0	12.1	41.8	7.3	4.6	7.4	0	0.9	13.8	2.1	18.6	45.2	8.6	1.14
6	450	1.2	5	18.3	33.7	3.2	2.2	36.7	2.1	0.8	11.1	1.3	12.7	30.0	6.1	0.10
7	450	1.2	10	14.0	31.8	6.3	2.8	8.1	0	0.8	25.0	1.7	16.3	39.0	8.8	0.78
22	350	2.6	0	13.6	47.4	0.6	1.3	7.4	0.1	0.1	10.2	0.2	22.9	57.3	2.0	0.19
24	350	2.5	10	12.1	48.8	0.6	1.2	6.3	0.2	0.1	21.8	0.1	21.3	48.3	8.3	0.21
12	400	2.5	0	9.8	55.4	0.2	0.3	4.3	0	0.1	4.2	0.1	33.5	57.4	11.6	0.08
25	400	2.6	5	10.4	45.3	0.3	0.4	2.1	0.1	0.1	4.0	0.1	35.7	57.2	15.9	0.25
16	400	2.5	10	8.2	50.2	0.7	1.3	7.8	0.3	0.2	20.4	0.3	20.0	49.0	8.3	0.19
21	450	2.7	0	11.4	45.0	2.4	2.5	7.6	1.2	0.4	8.6	0.8	20.6	55.9	9.0	0.47
23	450	2.5	10	11.4	41.3	1.5	1.4	4.7	0.7	0.3	11.8	0.1	25.0	54.5	11.8	0.45

In Table 4 the columns indicated coke %, tar % and C_5-C_{10} % give the mass percents of coke, tar and C_5-C_{10} in the overall products including coke and tar.

Figure 4 shows that the percentage of coke is mostly dependent on LHSV, generally decreasing as flow rate or LHSV in increased. This reflects a lower conversion to coke as the oil is contacted with the catalyst for a shorter residence time.

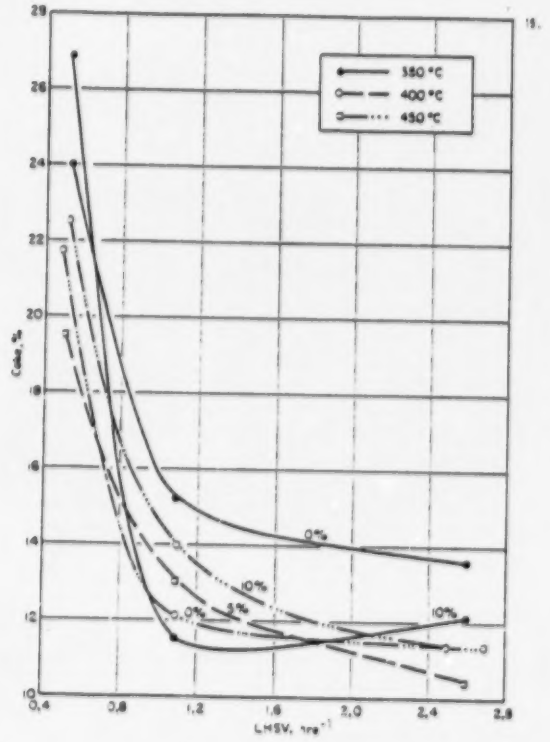

FIGURE 4. Percentage of coke as a function of the LHSV.

Figure 5 represents the percentage of the tar collected at 150°C as a function of temperature. It shows that the tar decreases with temperature at low LHSV and passes through a maximum around 400°C for the higher LHSV. Clearly the addition of methanol decreases the amount of tar produced, which indicates that methanol is participating as a reactant to the conversion of the oil.

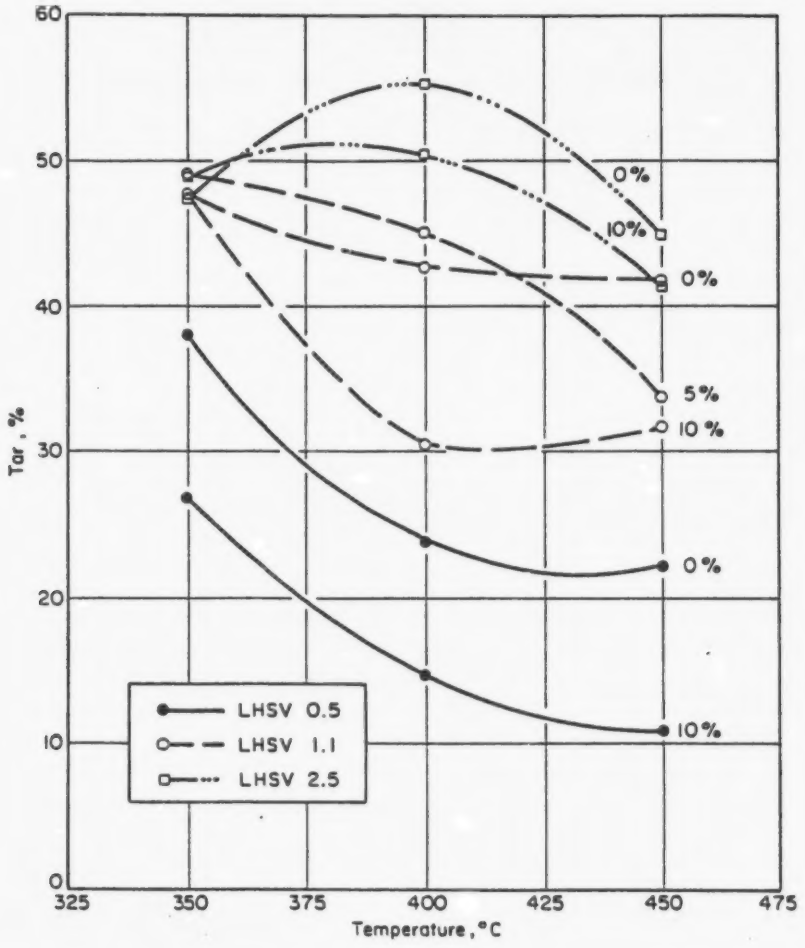

FIGURE 5. Percentage of tar as the function of the temperature.

Figure 6 shows that the C_5-C_{10} % is a complex function of LHSV with an initial decreasing branch corresponding to the decrease in conversion with a decreasing residence time. Most of the curves show also a minimum and a second increasing branch corresponding to the fact that although less oil is converted, a smaller fraction of the primary products is condensed to coke as shown in figure 4. Therefore the maximum values of C_5-C_{10} % observed at high LHSV are of more interest because although (as shown in Figure 5) the overall conversion is smaller more of the converted oil is transformed to hydrocarbon by avoiding the secondary reactions leading to coking.

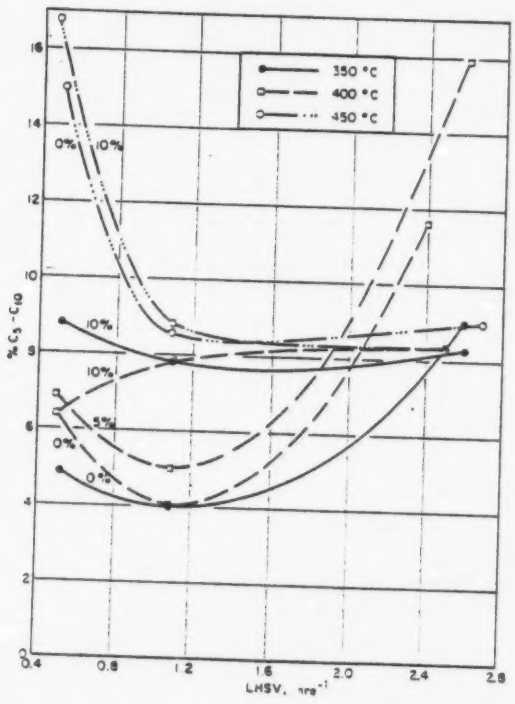

FIGURE 6. Percentage of hydrocarbon (C_5-C_{10}) as the function of LHSV.

Figure 7 reports the calculated values for the ratio:

$$Y = \frac{n_{O_2}(CO + CO_2)}{n_{O_2}(H_2O)}$$

where n_{O_2} $(CO + CO_2)$ stands for a number of moles of oxygen eliminated as CO or CO_2, whereas n_{O_2} (H_2O) represents the oxygen eliminated by dehydration. With pure methanol (expt. N° 1, Table 4) Y is of course close to zero since the MTG process is essentially a dehydration. As can be appreciated Y is strongly dependent on temperature and stands usually between 0.4 to 0.6 reaching exceptionally values higher than 1 at 450°C.

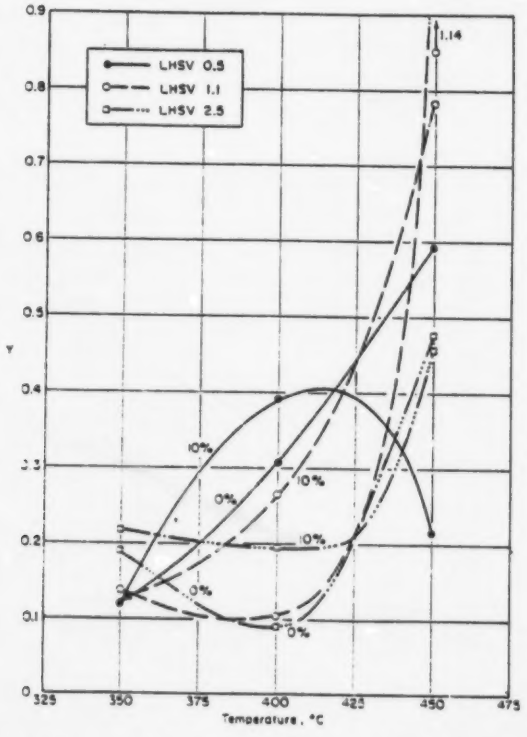

FIGURE 7. Value of Y as the function of the temperature.

Figure 8 gives some results obtained in another experimental set-up similar to the one described on Figure 1 but where trap N^{0} 3 has been replaced by a multiloop sampling valve. This allows the determination of the concentration with time for all uncondensable gases. This figure indicates a decrease in catalyst activity after 30 to 45 minutes on stream as shown by the decrease in alkanes and an increase in olefins concentrations.

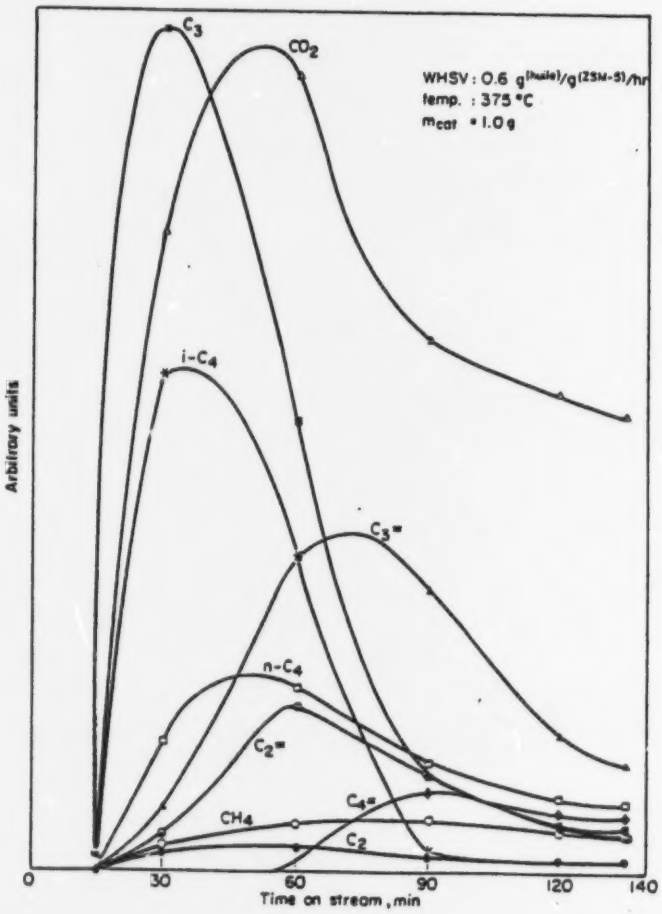

FIGURE 8. Analysis of the gaseous fraction collected in trap N^{0} 3 as a function of time for a run with indiluted ZSM5.

Figure 9 gives similar results obtained with a so-called embedded ZSM-5. We produced these solids by suspending small cristals (1 µm) of ZSM5 as a slurry in sodium silicate, and precipitating an amorphous silicagel by acidifying with an H_2SO_4 solution. The resulting solids contain approximately 25% of ZSM5.

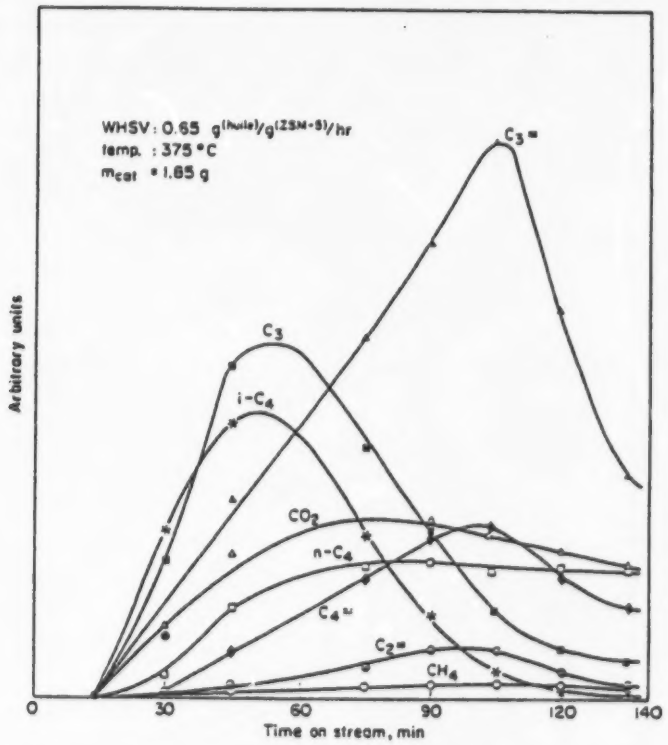

FIGURE 9. Analysis of the gaseous fraction collected in trap N° 3 as a function of time for a run with ZSM5 embedded in a silicagel.

This embedding technique is interesting because the bulky particles can now be fluidized and also because this technique is supposed to decrease coking which on ZSM5 is only possible on the external surface of the crystals (Rollman, 1979, Walsh and Rollman, 1979).

The experiment reported in figure 9 was conducted at a LHSV comparable to the one of the experiment of figure 8. (LHSV is calculated with respect to the volume of zeolite). The comparison of the results on both figures 8 and 9 show that this embedding technique increases the resistance to coking since the maxima in alkanes are switched from 30-45 to 60-75 minutes.

CONCLUSION

Our study shows that the simple method of contacting a pyrolytic oil with H-ZSM5 at temperatures 350-450°C is liable to convert 10-15% of the oil into C_5-C_{10} hydrocarbons. The most interesting conditions among those scanned are a temperature of 400-450°C and a LHSV of 2.5^{h-1}. The presence of some methanol has a beneficial effect on conversion of the oil. The coke formation is severe especially at low LHSV and can be improved by the so-called embedding technique.

With oil as a feed, unlike what is observed with methanol, a significant fraction of the oxygen removed is ending up as CO and CO_2 instead of water.

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NEW CATALYSTS FOR ALCOHOL CONVERSION INTO HYDROCARBONS: PRELIMINARY CATALYTIC TESTS ON CARBOHYDRATES

BY

R. LE VAN MAO, P. LEVESQUE AND P.H. BIRD
CONCORDIA UNIVERSITY,
DEPARTMENT OF CHEMISTRY,
1455 DE MAISONNEUVE WEST,
MONTREAL (QUEBEC),
H3G 1M8 CANADA,

ABSTRACT

By leaching the magnesium out of the chrysotile asbestos fibers and subsequently, crystallizing "in situ" the zeolite ZSM-5, catalysts for alcohol conversion into hydrocarbons were produced (Le Van Mao, R., and P.H. Bird, 1983). Surprisingly, they exhibited an enhanced shape selectivity when compared to the parent ZSM-5 zeolite (Le Van Mao, R., and P.H. Bird).

Product selectivities in the methanol reaction depended strongly on the magnesium leaching degree. Variations of this factor from 99% to 65% did not significantly affect the production of the liquid hydrocarbons but led to a large increase in the light olefin selectivity. Moreover, the gasoline boiling range products contained more aromatics and mono-branched hydrocarbons than those obtained with the equivalent ZSM-5 catalysts (Le Van Mao, R., and P.H. Bird). Finally, the ZSM-5/asbestos catalysts gave a higher proportion of ethylene than their ZSM-5 homologs.

We have extended our work to preliminary runs performed with sorbitol in aqueous solution.

Although sorbitol and its dehydrated derivatives are considered to be difficult to convert (Chang, C.D., et al), a composite ZSM-5/asbestos catalyst showed an interesting deoxygenating activity in terms of both overall activity and deactivation rate. The presence of increasing quantities of water in the feed reduced the rate of deactivation; however, some decrease in overall deoxygenating activity was also observed with increasing water amount in the feed.

The unique catalytic behaviour of the composite ZSM-5/asbestos might be a function of its non-acidic character combined with the low surface area of the asbestos macrostructure carrying the ZSM-5. Similar conclusions were drawn by Frankiewicz in his study of the ZSM-5 catalysts (Frankiewicz, T.C.).

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FINAL NOTES

FINAL NOTES

A review of the post-meeting discussion

The general discussion which followed the formal presentation of papers led to a prolific exchanges of views on: characterization of feedstocks and products, chemistry of liquefaction, engineering aspects associated with development units and wastewater treatment tests. A summary of the discussion is herewith presented:

- "Standard wood": comparison of yields and operational parameters among the different processes now sity to compare yields and operational parameters among the different processes now under development requires the definition and utilization of well characterized feedstocks. It is advisable that sponsoring agencies define a series of wood species, young and mature, normal or fast growing, which could serve as the basis for further comparative tests. Such a procedure would help to continue the effort of inter comparison of tests already started by the IEA working group on biomass liquefaction.

- Chemical events taking place during liquefaction: a mechanistic understanding of both the chemistry and the kinetics of liquid production from biomass is needed. Opposing viewpoints were expressed on the role of solvolysis versus thermal decomposition and the sequence of ultrastructural and chemical changes leading to the formation of low molecular weight intermediates. Also the role of acid/base catalysis which is particularly important in the low temperature range (130-250°C), needs to be further clarified and perhaps correllated with the general knowledge of pulping processes in either aqueous or organosolv media.

- Calculations on conversion and yields: the nature of the solvent used during the extractive sequence was the main cause of disagreement among different groups when comparing conversions and yields.

  A general consensus was established to report solvent-solubles rather than oil yields.

  The nature of the solvent needs to be specified. Common choices are: pentane, cyclohexane, chloroform, ether, tetrahydrofurane and acetone.

A second difficulty arises from the determination of water chemically associated with the oils. Its quantitative measure should not be done by the Dean-Stark method which is very susceptible to azeotrope formation but rather by the Karl Fischer titration technique. Even in this case verification via an alternate method (or comparison between two different laboratories) is preferred.

- Analytical consideration: considerable effort was reported on detailed fingerprinting methods derived from solvent fractionation and GG-MS techniques. Initial information on microscopic analysis was also presented. The link between this wealth of information and the mechnisms of liquefaction was not explored in any particular depth. Efforts to establish a relationship between fine product characterization and the chemistry of liquefaction are thus needed.

  A second analytical objective is the development of rapid techniques capable of defining steady state conditions in continuous systems as well as of being eventually used as markers for process control. On-line physical measurements like viscosity and density of slurries as well as on-line chemical analysis of selected products via G.C. or specific sensors is required for further process development.

- Engineering of new continuous approaches: although thorough explanations, and some discussion were offered by the authors concerning the descrip-tive aspects of their technological developments, there was little information on key process parameters,
  - heat transfer coefficients,
  - rheological data,
  - mixing patterns,
  - gas/liquid/solid ratios,
  - superficial velocities,
  - stress corrosion, materials.

  At this stage of techno-logical development each of the process developers appear to be concentrating on either constructing, commissioning or "making the machine work". Efforts to develop consistent material and energy balances followed by specific studies on the process parameters already mentioned (should be encouraged.)

- Upgrading of proto-oil: Two approaches are being followed based on either hydrorefining-type catalysts or H-ZSM5 preparations. Studies involve either the proto-oil, come of the fractions, or model compounds ressembling molecules present in the proto-oil. The information accummulated to date suggests that a significant fraction of the proto-oil can be succesfully converted into light hydrocarbon material using laboratory reactors. A high H_2 expenditure is however incurred during the upgrading. Catalysts lifetime and loss of activity are not known with any certainty. Furthermore, deoxygenation of the proto-oil which envolves H_2O formation with hydrorefining catalysts is accompanied by CO_2 formation when H-ZSM5 are used. This could be advantageous for lowering the H_2 consumption. No results are available on coke formation at extended operating periods.

A highlight of the meeting was the presentation by A. Oestman (group leader of the Biomass Liquefaction Working Group set-up by the IEA). He presented a summary of the findings which are to become public in mid 1984 in the form of the IEA report on Biomass Liquefaction.

The IEA study considered the fuel oil case only as the basis for comparison between processes. Tentative conclusions were presented by Anders as follows:

- research efforts by most groups have focussed on the central reactor either in pyrolysis or in direct liquefaction. Within a few years time most of the necessary phenomenological information on yields, operating conditions and catalytic preparations related to the central reactor should be established.

- Outside the central reactor there are an unusually large number of unknowns were influence the cost of the proto-oil they are:

(a) in high pressure direct liquefaction

a.1 recycling oil operation and need for solids separation

a.2 cost of needed H_2 (or CO/H_2)

a.3 catalyst recovery

a.4 gas-liquid-solids separation

a.5 feeding biomass at high pressure

a.6 heat transfer associated with heat exchanger design

(b) in pyrolytic systems

b.1 reactor uncertainties related to difficult scale-up criteria

b.2 heat transfer coefficients

(c) wastewater treatment is of common concern to both pyrolytic and direct liquefaction processor

(d) Product evaluation is a key area since it will determine the market value as a low or medium grade fuel

Technoeconomic analysis is also conducted by the IEA-Working Group. The basis for comparison is a 1000 BDT/day of biomass. In general pyrolysis routes have lower production costs than high pressure liquefaction products. In both cases the costs are higher than today's comparable petroleum-derived fuels. However, biomass derived proto-oil seems easier to upgrade than petroleum-derived gas-oils.

In summary, the Sherbrooke meeting provided a unique forum for exchange of scientific and technological information related to liquefaction processes. It is hoped that the collection of papers present in these Proceedings will serve as an stimulating basis for further advancements in the complex field of biomass liquefaction.

E. Chornet and R.P. Overend

LIST OF ATTENDIES

LIST OF ATTENDIES THIRD LIQUEFACTION EXPERTS MEETING

AFRASHTEHFAR, Shapour
Dept. of Chemical Engineering
McGill University
3480 University Street,
MONTREAL, Quebec
H3A 2A7

ANDERS, Ostman
Kemiinformation AB
Birkagatan 35
S-11339 STOCKHOLM
Sweden

AZIZ, Ahmed
Université Laval
QUÉBEC (Québec)

BECKMAN, David
Dept. of Chem. Eng. & Applied Chemist
University of Toronto
TORONTO, Ontario
M5S 1A4

BEDFORD, Linda
Département de chimie
Université de Sherbrooke
SHERBROOKE (Québec)
J1K 2R1

BERGSTROM, A.
Dept. Chemical Technology
Royal Institute of Technology
S-100 44 STOCKHOLM
Sweden

BJORNBOM, P.
Dept. Chemical Technology
Royal Institute of Technology
S-100 44 STOCKHOLM
Sweden

BOOCOCK, D.G.B.
Dept. of Chemical Engineering
University of Toronto
200 College Street
TORONTO, Ontario
M5S 1A4

BRIDLE, Trevor
Waste Water Technology Centre
Environment Canada
BURLINGTON, Ontario

CHANTAL, Pierre
Dept. Chemical Engineering
Laval University
QUEBEC, Québec

CHAUVETTE, Gaëtan
Université de Sherbrooke
405-2001, rue Dubreuil
SHERBROOKE, Québec
J1K 2R1

CHORNET, E. Dr.
Département de génie chimique
Faculté des sciences appliquées
Université de Sherbrooke
SHERBROOKE (Québec)
J1K 2R1

DANIEL, Jean
Université Laval
Québec (Québec)

DAO, Lê
INRS - Energie
Université de Québec
C.P. 1020
VARENNES, Québec
JOL 2PO

De CAUNIA, Bruno
Université de Sherbrooke
SHERBROOKE (Québec)
J1K 2R1

DeLUDE, S.G.
Shell Canada Ltd.
3415 Lakeshore Road, West
Box 2100
OAKVILLE, Ontario
L6J 5C7

DOAT, Jacqueline
Centre technique forestier tropical
45 bis av. de la Belle Gabrielle
94130 Nogent sur Marne
FRANCE

DOYON, Jacques
Département de génie chimique
Université de Sherbrooke
SHERBROOKE (Québec)

EAGER, R.L. Dr.
Dept. of Chemistry & Chemical
Engineering
University of Saskatchewan
SASKATOON, Saskatchewan
S7N OWO

EDWARDS, W.C.
B.H. Levelton & Assoc. Ltd.
8805 Osler Street
VANCOUVER, B.C.
V6P 4G1

ELLIOT, D.C.
Fuels & Mineral Technology Sectio
Battelle Pacific Northwest Laborat
P.O. Box 999
RICHLAND, WA
99352

EUGENE, Denis
Research Assistant
University of Sherbrooke
SHERBROOKE (Québec)
J1K 2R1

GAGNON, Jean
Dept. Chemical Engineering
University Laval
MONTREAL, Québec.

GRANDMAISON, J.-L.
Université Laval
QUÉBEC (Québec)

GRISÉ, Michel
Departement de chimie
Université de Sherbrooke
SHERBROOKE (Québec)
J1K 2R1

HÉBERT, Michel
Université de Sherbrooke
SHERBROOKE (Québec)
J1K 2R1

HÉBERT, P.
I.N.R.S - Énergie
Université du Québec
Case postale 1020
VARENNES (Québec)
JOL 2PO

HEITZ, Michèle
Université de Sherbrooke
SHERBROOKE (Québec)
J1K 2R1

HOGAN, Ed
Energy Mines & Resources
460 O'Conner Street
OTTAWA, Ontario

HOULE, Andrē
I.N.R.S. - Énergie
Université du Québec
Case postale 1020
VARENNES (Québec)
JOL 2PO

HOWARD, John Dr.
Division of Applied Chemistry
B.C. Research
3650 Wesbrook Mall
VANCOUVER, B.C.
V6S 2L2

HUFFMAN, D.R.
Forintek Canada Corp.
Eastern Laboratory
800 Montreal Roiad
OTTAWA, Ontario
K1G 3Z5

KALIAGUINE, S.C.
Dépt. de génie chimique
Université Laval
STE-FOY, Québec
G1K 7P4

KALLURY, K.M.R.
University of Toronto
Department of Chemistry
80 St. George Street
TORONTO, Ontario
M5S 1A1

KANNEL, A.
Dept. of Chemical Technology
Royal Institute of Technology
S-100 44 STOCKHOLM
Sweden

LABRECQUE, Raynald
I.R.E.Q.
1800 montée Ste-Julie
VARENNES (Québec)
JOL 2PO

LALANCETTE, Andrē
Université de Sherbrooke
SHERBROOKE (Québec)
J1K 2R1

LEEN, K.
CRIQ
333 rue Franquet
Box 9038
STE-FOY, Qubec
G1V 4C7

LÉGER, Sylvain
Université de Sherbrooke
SHERBROOKE (Québec)
J1K 2R1

LE VAN MAO, R.
Concordia University
1455, de Maisonneuve W.
Montreal, Quebec
H3G 1M8

LEVESQUE, P.
Concordia University
1455 de Maisonneuve W.
MONTREAL, Quebec
H3G 1M8

LOPEZ-SANTIN, José
Université de Sherbrooke
SHERBROOKE (Québec)
J1K 2R1

MAHAY, Arnaud
Dept. Chemical Engineering
Laval University
QUEBEC, Québec

MARTEL, Anna
Departement de chimie
Université de Sherbrooke
SHERBROOKE (Québec)
J1K 2R1

McDONALD, E.C.
Division of Applied Chemistry
B.C. Research
3650 Wesbrook Mall
VANCOUVER, B.C.
V6S 2L2

McKEOUGH
Fuel and Lubricant Research Lab.
Technical Research Centre of Finland
02150 ESPOO 15
Finland

MÉNARD, Hugues
Département de chimie
Université de Sherbrooke
SHERBROOKE, Quebec
J1K 2R1

MOFFATT, J.M. Dr.
SNC. Inc.
1 Complexe Desjardins
C.P. 10
MONTREAL, Québec
H5B 1C8

PISKORZ, Jan
Dept. of Chemical Engineering
University of Waterloo
WATERLOO, Ontario
N2L 3G1

POIRIER, Michel
Université Laval
QUÉBEC (Québec)

ROY, Christian
Dépt. de génie chimique
Fasculté des sciences appliquées
Université de Sherbrooke
SHERBROOKE, Québec
J1K 2R1

SCOTT, D. Dr.
Dept. of Chemical Engineering
University of Waterloo
WATERLOO, Ontario
N2L 3G1

SOYER, Noël
École nationale supérieure
de chimie de Rennes
(E.N.S.C.R.)
Avenue du Général Leclerc
35000 Rennes-Beaulieu
FRANCE

SWAN, Eric
Forintek Canada Corp.
VANCOUVER, British Columbia

TIDWELL, T.T.
Department of Chemistry
University of Toronto
TORONTO, Ontario
M5S 1A1